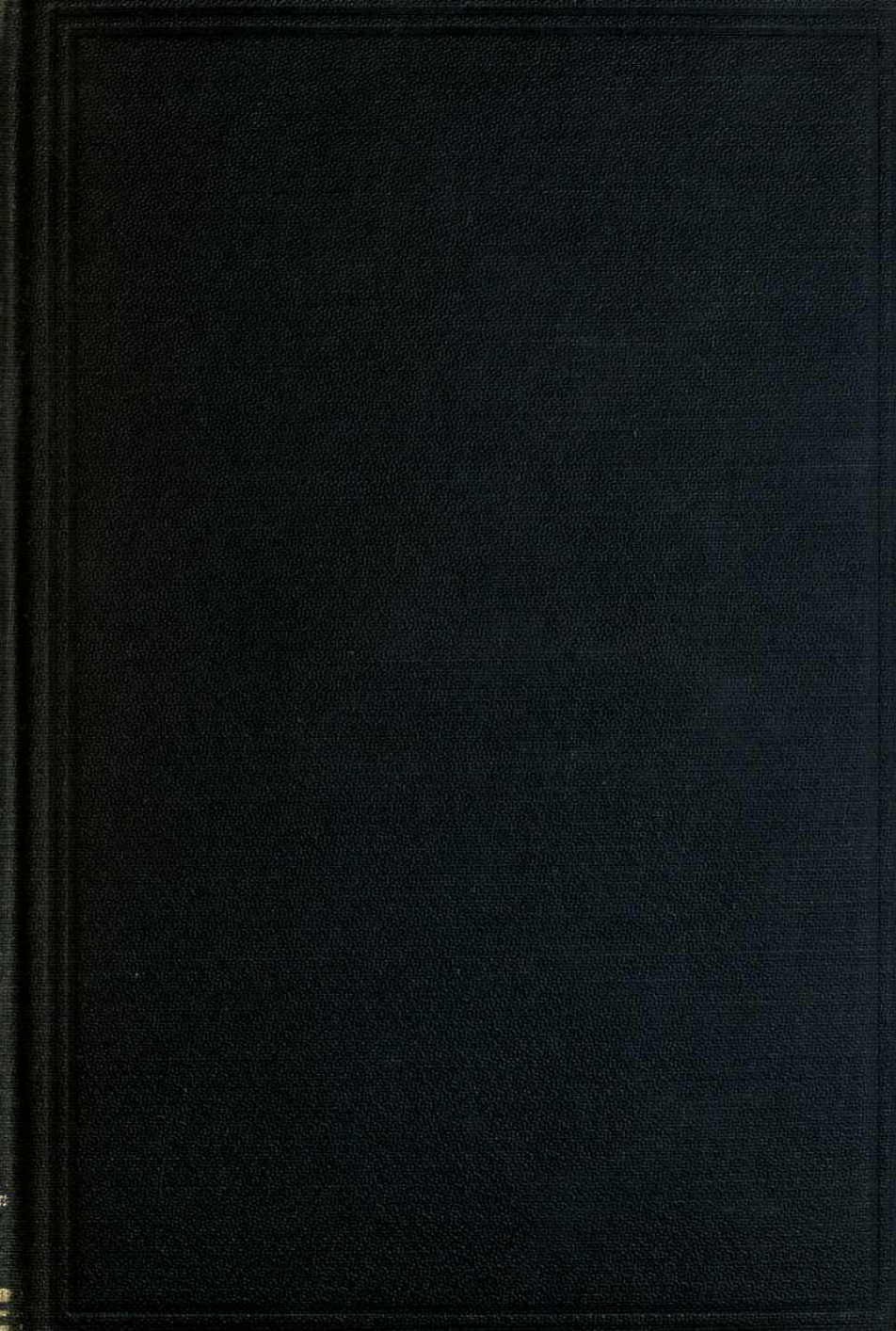
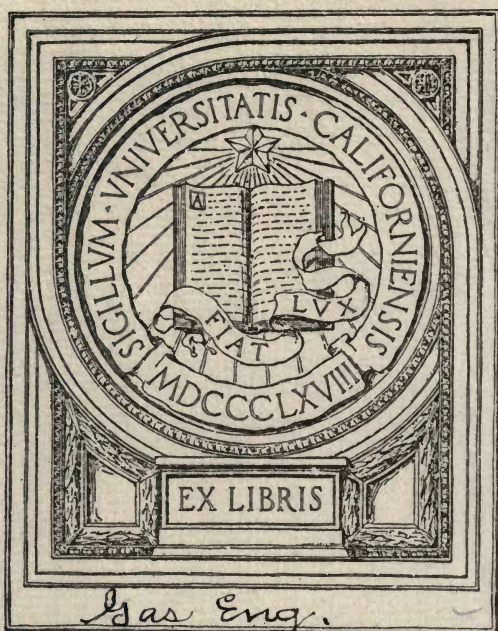






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GAS ANALYSIS



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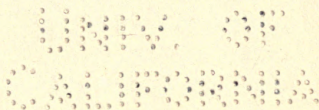
TORONTO

GAS ANALYSIS

BY

L. M. DENNIS

PROFESSOR OF INORGANIC CHEMISTRY
IN CORNELL UNIVERSITY



New York

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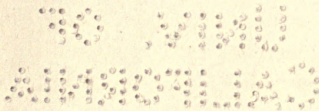
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PREFACE

In general plan this book follows the last edition of the English translation of Hempel's *Methods of Gas Analysis*. It was indeed begun with the intention of having it serve as a new edition of that work, but the many advances in the field of gas analysis during the last fourteen years have necessitated the incorporation of much new material and the modification or excision of many of the older methods. In view of this fact, a new book has been written.

With the kind permission of Professor Hempel, full descriptions of his classic methods for both technical and exact gas analysis have been incorporated in the present work, although in some cases the apparatus and the manner of its manipulation have been modified.

Procedures for the determination of most of the gases that will be met with in analytical work are given in considerable detail. Although no attempt has been made to include descriptions of all of the new methods that have recently appeared, references to original articles are given throughout the work in order to assist the reader in obtaining more complete information upon the various topics than could be included in a laboratory manual.

The separation of the gases of the argon group has not been discussed for the reason that rapid and simple analytical methods for the determination of these several gases have not as yet been perfected.

Certain methods of exact analysis that are adapted to specific determinations have been described, but the greater part of the book is devoted to rapid methods of technical gas analysis because it is in this division of the field that most of the work of the gas analyst will lie.

In gas analysis the accuracy of the determination is probably dependent to a greater degree upon the manipulatory skill with which the work is performed than in any other branch of chemical analysis. It is for this reason that the manipulation of each of the more generally used types of apparatus is described at length.

I desire here gratefully to acknowledge the assistance that has been given me by my colleague Dr. R. P. Anderson to whom I am indebted not only for the preparation of the greater portion of the chapter dealing with the combustion of gases, but also for many valuable suggestions and for a careful reading of the proof-sheets. I take pleasure also in expressing my indebtedness to Mr. F. H. Rhodes for his skillful assistance in the testing of several of the new methods of analysis that are here described.

L. M. DENNIS.

ITHACA, NEW YORK,
February, 1913.

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GAS ANALYSIS

CHAPTER I

THE COLLECTION AND STORAGE OF GASES

Drawing off the Sample. — The collection of a sample of gas from a pipe, conduit, or furnace is usually accomplished by inserting into the chamber a tube of suitable material and drawing off the gas either into a sampling tube or bottle, or directly into the apparatus in which the gas mixture is to be analyzed. If the gas is at a comparatively low temperature, it may be drawn off through a tube of glass, and this material or porcelain must of necessity be employed if the gases are of an acid character. At temperatures below 300° a small lead pipe will be found convenient because of its flexibility. At higher temperatures iron, porcelain, or quartz tubes may be used. If the gases are very hot, the tube should be surrounded by a second tube through which cold water is kept circulating.

A satisfactory form of such a tube is that described by Winkler in 1885.¹ It consists of the tubes *A*, and *C*, Fig. 1, and a third tube, lying between *A* and *C*, to which the side arm *B* is attached. The tubes are made of metal, either copper or iron being usually employed.² The tube *A*, through which the gas sample is drawn, is about 5 mm. internal diameter. The tubes are kept cool by running water which enters through *B*, flows through *C* and escapes through the outlet *D*. A tube of glass or lead carrying a short side tube is attached to *A*, and

¹ *Lehrbuch der technischen Gasanalyse*, 1st ed., p. 9.

² Frazer and Hoffman, *Bulletin 12, Bureau of Mines*, suggest the use of an inner tube *A* of quartz.

its further end is connected with an aspirator. The sample of gas to be analyzed is drawn off through this tube into the sampling tube or gas burette, as desired.

Gas mixtures that are to be subjected to chemical analysis should never be passed through long pieces of rubber tubing. Rubber is not only porous, but it may also absorb certain constituents of the gas mixture. These absorbed gases or even the air that a fresh piece of rubber tubing contains will cling tenaciously to the walls of the tube, and when a gas mixture of other composition is passed through the tube they will slowly but continuously mix with the entering gas. If for any reason the use of a long piece of rubber tubing cannot be avoided in the collection or transfer of a sample of gas, the rubber tube should be vigorously rolled between the palms of the hands while the

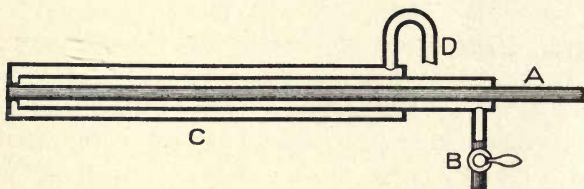


FIG. 1

sample is flowing through it, in order to detach the gas adhering to its walls. The gas that passes through the tube during this operation should of course be discarded.

When short pieces of rubber tubing are used for connecting tubes of other material, the ends of the tubes should be brought together under the rubber connector.

A sample of the gaseous products of combustion from a heating apparatus should be drawn from the back of the fire chamber: further up in the flue the gas will usually be found to contain a considerable quantity of air because of the porosity of the wall.

A gas mixture flowing through a pipe is frequently of varying composition from the middle of the pipe toward its sides. For

this reason the sample tube that is inserted into the gas main should extend across the pipe or channel from side to side and have a fine longitudinal slit or a series of small holes throughout nearly its entire length in the main so that the sample drawn off will show as nearly as possible the average composition of the gas.¹

Sampling Tubes.— If the place where the gases are to be collected is directly accessible, as, for example, in the examination of mine gases, small sampling tubes made in the laboratory from easily fusible glass tubing may be employed. The form used by Hempel in his researches “upon the composition of the atmosphere at different parts of the earth” is shown in Fig. 2. *d* is about 4 mm. thick; *a*, *b*, and *c*, only 1 mm. These tubes were heated in an air bath in the laboratory to 200°, and were then



FIG. 2



FIG. 3

exhausted with a mercury air-pump and fused at *c*. By simply breaking the tube at *b*, it fills instantly and completely with the air in question. The tubes are then closed for a few moments with a rubber cap, and are sealed off at *a* over a candle. The exhausting with the air-pump has the advantage of rendering one less dependent upon the care of the person who fills the tubes. If, however, it is desired to avoid this exhausting, the tubes are given the following form (Fig. 3). To fill such a tube, the gas to be examined is drawn through it and the tube is then sealed at *a* and *b* by fusion in a candle flame.

Such tubes can safely be shipped by packing them in sawdust in boxes that have a separate compartment for each tube. The boxes themselves are placed in a larger box filled with hay.

A somewhat more convenient tube for collecting gas samples and transporting them to the laboratory for analysis is that

¹ See *Metallurgical and Chemical Engineering*, 9 (1911), 303.

shown in Fig. 4. The tubes used in the Cornell laboratory vary from 16 cm. x 3.5 cm. (capacity about 110 cc.) to 25 cm. x 4.5 cm., the stopcocks have a bore one mm. in diameter, and the tube ends beyond the stopcocks are capillary tubes of six mm. external diameter, one mm. bore, and about four cm. long. If the stopcocks are well made and carefully lubricated, and are fastened securely in place after the tube is filled with the gas, a sample may be kept for a considerable length of time in such a tube without undergoing appreciable change, provided the gas mixture does not act upon the lubricant of the stopcocks.

In equipping a laboratory it is also well to provide some of these sampling tubes with tailstoppers (Fig. 5). Such stop-

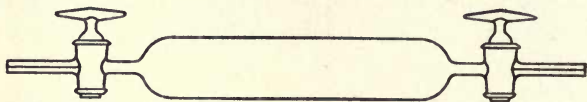


FIG. 4

cocks render easy the elimination of the dead space in the end capillary tubes when the sample is transferred to the gas burette (see p. 59)

but as they are more liable to leak than are the single bore stopcocks, tubes that are fitted with them, while more useful in the laboratory, are not so well suited to the transport of gas samples.

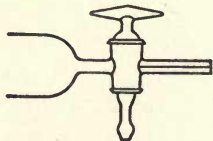


FIG. 5

These tubes are filled with the gas sample by drawing it through the tube until the air that was originally in the tube is entirely displaced. Naturally this presupposes that large amounts of gas are at one's disposal. If only a small quantity of gas is available, the tube is first filled with water or mercury and this is then displaced by the gas. Water can be used only when it is first saturated with the gas mixture that is being sampled and if any of the constituents of the gas mixture are

fairly soluble in water, as, for example, ammonia or carbon dioxide, mercury must be employed even if only approximately accurate results are desired.

It is frequently the case that an average sample of the gases passing through a flue or pipe during a period of several hours is desired. Since carbon dioxide is always present in flue gases, mercury must be used as the confining liquid in the sample tube. The weight and costliness of mercury make it necessary that the sample tube be small, and this in turn renders it imperative that the dead space between the sample tube and main tube be eliminated and that it be impossible for the gas in the sampling tube to diffuse back into the main tube or to be drawn back into the main by a sudden drop in the pressure. These conditions are fulfilled by the clever device of Huntly¹ which is shown in Fig. 6. The tube² is first filled with mercury up to the top of the bore of the upper stopcock, and both stopcocks are closed. The capillary *A* is then connected with the branch from the main tube, and the stopcock turned so that *A* communicates with *B*. The air in *A* is thus driven out through *B*. If the pressure in the main is less than that of the atmosphere, suction must be applied at *B*. The upper stopcock is then turned through 180° to connect *A* with *C*, and the lower stopcock is carefully opened to such an extent as will give the desired speed of flow. Huntly states that "it has been found by trial that the rate at which the gas is drawn in is constant throughout within one per cent."

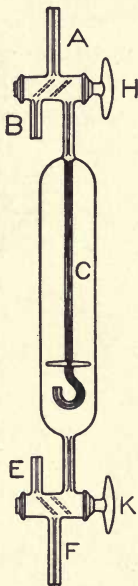


FIG. 6

¹ *J. Soc. Chem. Ind.*, 29 (1910), 312.

² Huntly does not give the dimensions of the tube. If the wide part of the tube were about 18 cm. long and 3.5 cm. diameter, it would contain quite a little more than 100 cc., an amount sufficient for the analysis.

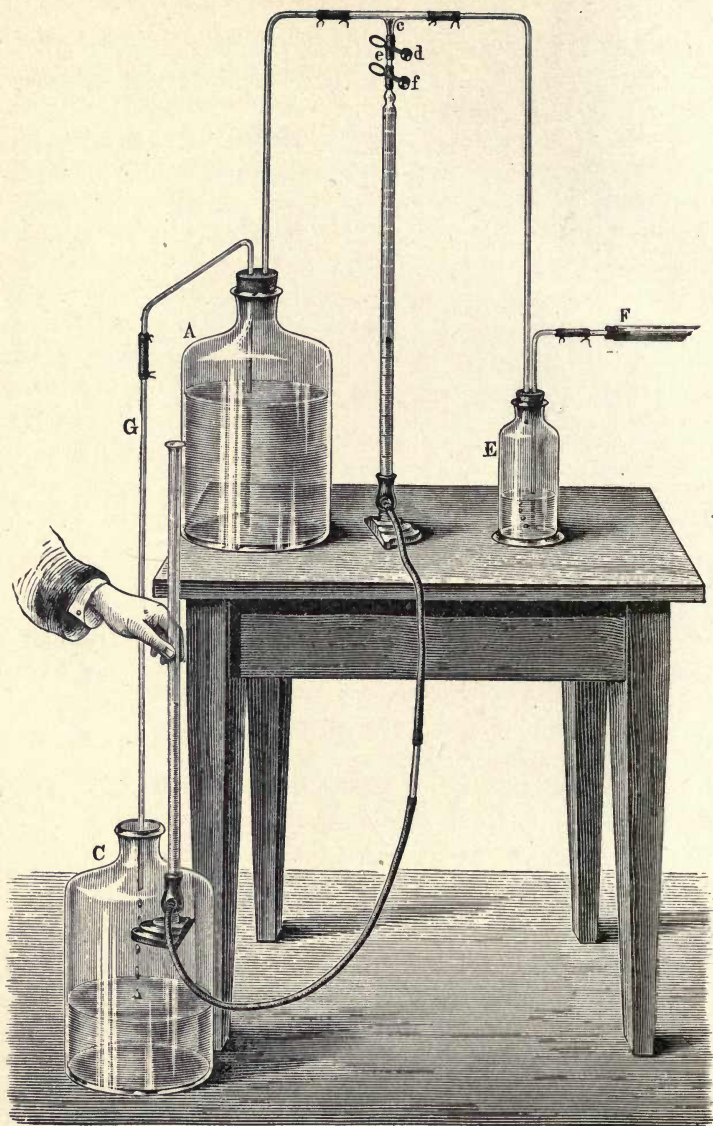


FIG. 7

If the tube is to be shipped to the laboratory after the sample has been taken, some mercury should be left in the capillary tube above the stopcock *K*, and the tube should be placed in a frame that will support it in an upright position.¹

Aspirators. — If the gases to be collected have a pressure less than the prevailing atmospheric pressure, an aspirator must be employed to draw them over into the sampling apparatus. The simplest form of aspirator consists of two interchangeable bottles of equal size and of the same width of neck. If it is desired to draw off a sample of gas for analysis while the mixture is being aspirated the arrangement shown in Fig. 7 may be employed. The water flows from the bottle *A* through the siphon tube *G* into the lower bottle *C*, and by so doing draws the gas through the tube *F*. When the bottle *A* is empty *C*, which is now full, may be put in its place and the aspirating of the gas continued. The gas burette is connected to a T-tube in the manner shown,



FIG. 8

is filled to the horizontal tube at *c* by opening the pinchcocks *d* and *f* and raising the level-tube, and is then filled with a sample by lowering the level-tube to the position shown in the figure. The pinchcocks *d* and *f* are then closed and the rubber tube attached to the burette is slipped off from the small glass tube *e* which joins the two short pieces of rubber tubing.

Small rubber suction bulbs, Fig. 8, may at times be found useful for drawing a gas mixture into the sampling tube, which

¹ In *Bulletin No. 12 of the Bureau of Mines* (1911) Frazer and Hoffman describe a sampling tube that is patterned after that of Huntly, but is inferior to the latter in that it does not carry the double stopcocks which facilitate the elimination of the dead space in the capillary tubes.

should be placed before the bulb to avoid contact of the rubber with the gas. If running water is available, a water suction pump of glass (Fig. 9) or the more compact and durable Chapman pump of brass, may be used for this purpose.

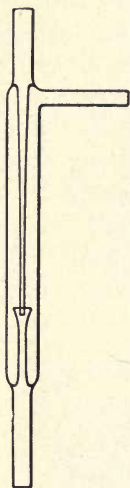


FIG. 9

pump in that stronger suction is obtained and the bulb does not come in contact with the gases which, if of corrosive nature, would soon destroy it.

With such an apparatus as that constructed by Körting,² steam also may be used for aspirating.

The Mercury Pump. — A mercury pump is at times needed for the exhaustion of sample tubes like those described on p. 3, and for the removal and collection of gases in certain operations

If running water is not at hand a suction pump and rubber pressure bulb may be used for drawing the gas through the apparatus. Fig. 10 shows such an arrangement,¹ the rubber pressure bulb being here attached to a Finkener suction pump. The rubber tube on the side arm of the pump is joined to the apparatus through which the gas is to be drawn. This device is superior to the rubber suction

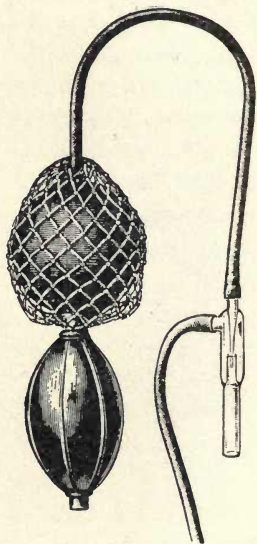


FIG. 10

¹ Offerhaus, *J. f. Gasbeleuchtung*, 53 (1910), 806.

² Gebr. Körting Akt.-Ges., Körtingsdorf near Hanover.

such as that described on p. 22. Of the many forms of mercury pumps that have been designed, that of Töpler is one of the most satisfactory. The construction and operation of the pump have been clearly described by Travers, from whose book on the "Experimental Study of Gases" the following description is quoted:

"The Töpler Pump. — The pump-chamber *A* (Fig. 11) is made of stout glass, and should be about 200 mm. long and 50 mm. in diameter; the ends, and particularly the upper end, should be tapered considerably to meet tubes of about 13 mm. in diameter. If the upper end of the pump-chamber presents a surface approaching to the horizontal to the mercury as it rises to the pump-head, films or even bubbles of air may be entrapped between the mercury and the glass, and exhaustion will be slow. The side-tube which joins the vertical tubes at *F* and *H* should also be of about 13 mm., diameter; the internal angle between the two tubes at the upper junction should, for the reasons given above, be very acute. The tube *C*, through which the gas enters the pump, should be much narrower than the side-

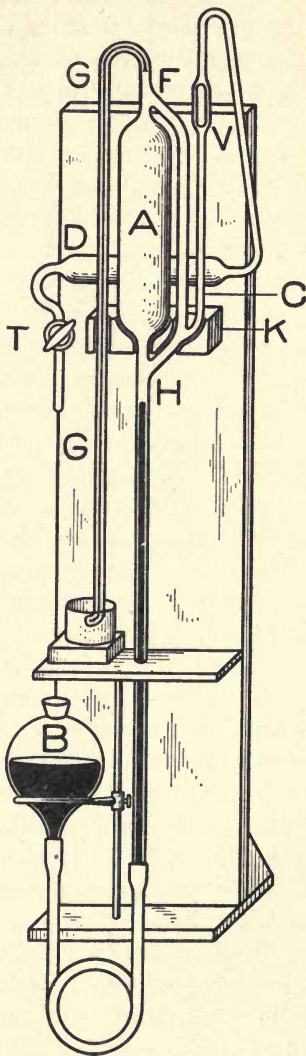


FIG. 11

tube, 4 mm. is a convenient diameter; if it is not made so the gas which enters the pump while the mercury is still falling, may carry the whole of the mercury in the side-tube into the upper part of the pump, and cause a serious fracture. If the pump is properly constructed, the gas will rise in bubbles between the mercury and the glass.

"The vertical tube *F* at the top of the pump-chamber, should be tapered to meet the capillary tube *G*, which should be bent on itself in a continuous curve of about 3 cm. in diameter immediately above this point. The length of the capillary tube should be about 800 mm., and its internal diameter should not much exceed one mm.; it should be turned up at its lower end so as to admit of collecting gases through the pump. The capillary tube may easily be replaced when broken if a sufficient length of tube is left above the junction at *F*. A piece of tube, of the same diameter as the vertical tube of the pump, is first sealed to a straight piece of capillary tube of sufficient length. The tube is worked in the blowpipe flame till a perfectly even tapered junction is obtained; it is then bent, cut to the right length, and sealed to the pump-head with the aid of a small blowpipe. The efficiency of the pump will depend to a great extent on the care which is expended on this part of it.

"The lower vertical tube should be so long, about 800 mm., that when there is a vacuum in the pump and the mercury stands below the level of the joint *H*, the lower end of it lies below the level of the mercury in the reservoir, or air may slowly leak into the pump through the junction with the rubber tube. The rubber tube should not be longer than is necessary to allow of the reservoir being raised to the level of the pump-head, and its internal diameter should be nearly as large as that of the glass tube to which it is attached so as to allow of the free flow of the mercury. In order to obviate any chance of the rubber tube bursting, it should be sewn into a strip of leather or inclosed in a piece of hollow cotton lamp-wick.¹

¹ These precautions are quite unnecessary if enamelled rubber tubing is employed.

"In order to prevent the mercury from passing into the tube *D*, containing pentoxide of phosphorus, when the reservoir is raised, the tube *C* may be carried vertically upwards to a height of about 900 mm. and then bent on itself. It is more convenient, however, to employ a glass valve *V* as in the figure, and it is probable that the rate of exhaustion of a piece of apparatus attached to the pump would be considerably decreased by the interposition of the long glass tube. The valve should be ground so that its upper surface fits sufficiently accurately into the inner surface of the tube containing it to hinder the passage of the mercury; the angle between the two surfaces should be very obtuse, or the valve may tend to remain closed after the mercury has fallen. The top of the valve should be on a level with the junction *F* (Fig. 11), so that the mercury closes it before it reaches the capillary tube.

"The tube *D* containing the pentoxide of phosphorus¹ is usually connected with a large two-way stopcock *T*, so that the pump may be used in connection with more than one piece of apparatus.

"The pump may be fixed to a stout board as in the figure. The block *K* is cut so that the bottom of the pump-chamber rests on it, and is kept in place by means of a strip of brass and a couple of screws.

"The fall-tube passes through a hole in the bottom of the tray; a cork fitting closely to the fall-tube serves to keep it firmly in place, and to prevent the escape of mercury through the hole. The tray supports the basin into which the end of the capillary tube dips. The board to which the pump is

¹ This reagent is almost universally used as a dehydrating reagent in working with gases, but it is somewhat difficult to obtain pure. The oxide should be perfectly white and quite free from discolored nodules and sticky masses of metaphosphoric acid. When exposed to the air it should deliquesce without turning red or giving off any odor. The principal impurities consist of the lower oxides of phosphorus, some of which are in themselves volatile and react with gases, such as chlorine and ozone, and with water vapor to yield phosphoretted hydrogen. The pentoxide can be obtained absolutely free from the lower oxides by throwing it into a red-hot porcelain basin, and stirring it in a current of oxygen.

attached may be screwed to the wall at a convenient height, or fixed to a stand.

"The reservoir may be placed in a bracket, or supported in a retort ring with a piece cut out of it to allow of the passage of the rubber tube. The retort ring may be fixed to an iron rod passing through holes in the tray and stand. A pulley and cord may be found convenient in working large pumps.

"Method of Working the Töpler Pump.— The pump is first carefully cleaned with chromic and sulphuric acids, washed with distilled water and alcohol and dried. It is then set up on the stand, the tube *C* is sealed to the tube *D*, containing pentoxide of phosphorus, and the rubber tube and reservoir *B* are attached. When sufficient mercury has been poured into the reservoir and trough the pump is ready for use.

"The reservoir is raised so as to expel about two-thirds of the air in the pump-chamber through the capillary tube, and is then lowered. As the mercury falls the air in the tube containing the pentoxide forces its way through the mercury in the side tube, and enters the pump. The operation is then repeated, but during the first few strokes the air should not be completely expelled from the pump-chamber. If this precaution is not taken the air will begin to enter the side-tube, while it still contains a long column of mercury; it will not then break up into bubbles, but will probably carry the whole of the mercury upwards against the junction *F* causing a serious fracture. On no account should the tap *T* be opened while the mercury is falling in the pump-chamber, or a similar accident may result. In any case the gas should only be allowed to enter the pump slowly. A rapid current of gas may impact the pentoxide of phosphorus into the end of the tube containing it, and render subsequent exhaustion very slow.

"During the last stages of the process of exhaustion care must be taken that the mercury does not come into violent contact with the top of the pump, or a fracture may result. The mercury may be allowed to rise rapidly to the junction *F*; it may then

be checked either by pinching the rubber tube or by lowering the reservoir. With practice the action becomes automatic.

"When a pump is first set up it should be allowed to remain exhausted for a sufficient time for the complete absorption of water in the apparatus by the pentoxide of phosphorus. Further, since gases like carbon dioxide condense in considerable quantity on glass surfaces, the maximum efficiency will not be reached till the pump has been filled with air, and exhausted two or three times."

Collection of Gas from the Mercury Pump.

— The method described by Travers for collecting the gases that are drawn by the pump from a container consists in filling a tube with mercury and inverting this over the end of the capillary tube *G*. According to Keyes¹ this procedure is open to objection because there is always present between the mercury and the walls of the connecting tube, a film of air that cannot, in the Travers' method of manipulation, be removed from the tube before the gas sample is driven into it. To remedy this difficulty

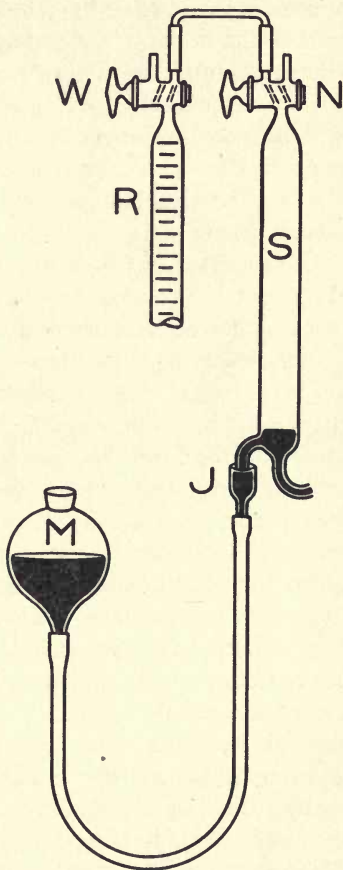


FIG. 12

Keyes fuses the sampling tube *S*, Fig. 12, to the upturned end of the capillary tube *G*, Fig. 11. A small trap *J* is fused to

¹ *J. Am. Chem. Soc.*, 31 (1909), 1271.

the lower end of *S* and this is connected to the level-bulb *M*. At the upper end of *S* is a double-bore stopcock *N*. If the mercury pump is to be used simply to exhaust a container, stopcock *N* is left open to the air with the mercury standing at the level shown in the figure during the first few strokes. When the exhaustion of the apparatus is nearly complete, the level bulb *M* may be raised to expel the air from the tube *S*. The stopcock *N* is then closed and upon lowering the level bulb a fair vacuum will result in *S* which will facilitate the escape into this tube of the bubbles of gas passing downward through the capillary tube of the pump.

To collect the gas that is discharged from the pump the tube *S* is connected to a gas burette *R* by a bent capillary tube and short connectors of rubber tubing in the manner shown in the figure. Mercury is used as the confining liquid in *R* as well as in *S*. The level tube of the burette *R* is raised and the air in the burette is driven over into the collecting tube *S*. The stopcock *W* of the burette is then closed and the air adhering to the walls of the burette is caused to collect at the top of the tube by lowering the level tube of the burette and thus bringing the tube under diminished pressure. The air thus released is expelled from the burette by raising the level tube and opening the stopcock *W*. The air in the collecting tube *S* is driven out by first raising the level bulb *M* and driving out most of the air in the tube through the bore of the stopcock *N* that communicates with the open air. *N* is then closed, the level bulb is lowered, and the air thus liberated from the walls of the tube *S* is driven out through the stopcock by raising *M*. Upon repeating these operations several times the collecting tube and the gas burette may be rendered practically free from gas (air). The mercury pump is now started and the gas to be collected is driven over directly into the tube *S*. At the conclusion of the pumping this gas is passed over into the burette *R* by raising the level bulb *M* and turning the two stopcocks to the proper positions. Any minute gas bubbles that may have lodged

between the mercury and the glass walls can easily be set free and recovered by the manipulation above described.

Collection of Gases from Springs.—To collect gas from springs that are directly accessible, the small apparatus proposed by Bunsen¹ may be used (Fig. 13).

This consists of a test-tube *c* of from 40 to 60 cc. capacity, drawn out at *a* before the blast-lamp to the size of a fine straw, and connected air-tight with the funnel *b* by means of a well-fitting cork or a piece of rubber tubing. The apparatus is then filled with the water of the spring. This cannot be done without access of air, which would change the composition of the gases dissolved in the spring water in the tube. Hence the inverted apparatus, with the mouth of the funnel upward, is lowered below the level of the spring, and, with a narrow tube reaching to the bottom of the test-tube, the water that in the first filling had come in contact with the air is sucked out until one is satisfied that it has been entirely replaced by other water from the spring. If now the gas of the spring is allowed to rise through the funnel into the test-tube thus filled, the purity of the sample is assured. If the rising bubbles stop in the neck of the funnel or at the contraction *a*, they can easily be made to ascend by tapping the edge of the funnel upon some hard substance. The apparatus is then placed in a small dish and removed from the spring, and the tube is sealed by fusion at *a*. This can easily be done with the blow-pipe, the moisture at the point *a* having first been driven away by warming.

W. Ramsay and M. W. Travers² have proposed the apparatus

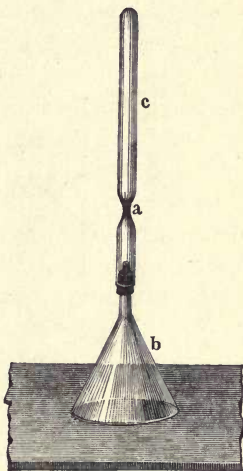


FIG. 13

¹ Bunsen, *Gasometrische Methoden*, 2d ed., p. 2.

² *Proc. Royal Soc., London*, 60 (1896). 442.

shown in Fig. 14 for collecting large quantities of gases from mineral waters. The cylinder *A* is filled with the water of the spring, and the rising bubbles of gas pass into the cylinder through the funnel *D* and the tube *C*.

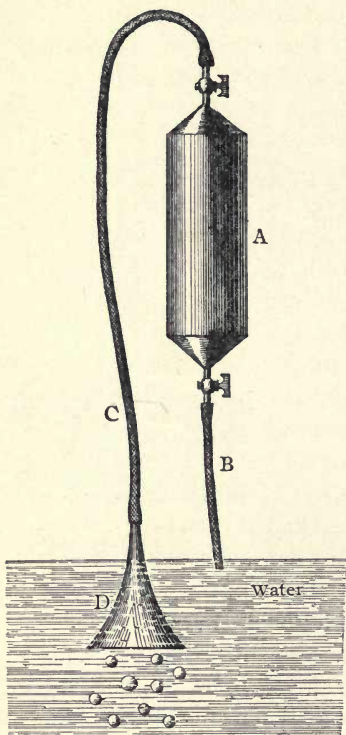


FIG. 14

slightly bent tube that can be closed with the rubber tube and pinchcock *g*. In the lower end of *C* is a rubber stopper with two holes through one of which the tube *bc*, projecting about 80 mm. into *C*, is inserted. Though the other opening passes the tube *d* which extends only slightly beyond the stopper

Collection of Gases dissolved in Liquids. — For the determination of the volume and composition of the dissolved gases in liquids, the Tiemann and Preusse modification of Reichardt's apparatus¹ can be recommended (Fig. 15).

This consists of two flasks *A* and *B*, each of about 1 liter capacity, and connected by tubes with the gas-collector *C*. The flask *A* is fitted with a perforated rubber stopper in which is inserted the glass tube *a* bent at a right angle and ending flush with the lower surface of the stopper. *a* is joined by a piece of rubber tubing to the tube *bc*, which in turn connects with the gas-collector *C*. *C* is held by a clamp, has a diameter of 35 mm., is about 300 mm. long, and at the upper end is drawn out to a short, narrow, and

¹ *Berichte der deutschen chemischen Gesellschaft*, 12 (1879), 1768.

and connects *C* with the flask *B*. *B* has a double-bore rubber stopper carrying the tubes *e* and *f*. *e* ends about 10 mm. above the bottom of the flask, and above the stopper it is bent at a right angle and is connected with *d*. The tube *f*, which need not project below the stopper, carries a thin rubber tube *x* about 1 m. in length and provided with a mouthpiece. A pinchcock for closing the rubber tube between *a* and *b* is also needed.

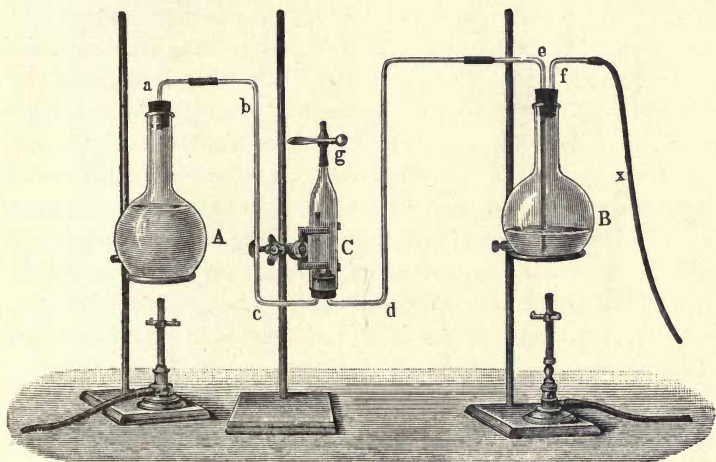


FIG. 15

The apparatus thus arranged is made ready for a determination by filling the flask *B* somewhat more than half full of boiled water and removing the flask *A* by slipping the tube *a* out of the rubber connection; then, by blowing into the rubber tube *x*, water is driven over from the flask *B* into the gas-collector *C* and the adjoining tubes, until the air is wholly displaced. The rubber tubes at *b* and *g* are now closed with pinchcocks. The flask *A* is then filled to the brim with distilled water, the stopper is inserted, water being thereby driven into the tube *a*, and the flask is again connected with *b*, the pinchcock being opened.

The water in *B* is now heated to gentle boiling, and that in *A* is allowed to boil somewhat more rapidly. The absorbed air is thus driven out, and the gases which are dissolved in the water in *A* and *C* collect in the upper part of *C*, from which they are removed by occasionally opening the pinchcock at *g* and blowing into the rubber tube *x*.

When, upon cooling the apparatus, the gases that have collected disappear, the heating of the flask *A* is discontinued, the pinchcock between *a* and *b* is closed, and *A* is disconnected and emptied. The water in *C* and *B* is now entirely free from absorbed gases, and air cannot enter from without because the liquid in *B* is kept continually boiling. The apparatus is now ready for a determination, which is made as follows:—

The cooled flask *A*, whose capacity has previously been determined, is filled with the water to be examined, and the stopper is pressed in so far that the air in the tube *a* is completely driven out. *a* is then connected with *b*, care being taken that in so doing no air-bubbles are inclosed. The pinchcock between *a* and *b* is opened, and the water in *A* is heated to gentle boiling. The dissolved gases are hereby driven over into the gas-collector *C*. Steam is formed at the same time. The heating of the flask *A* must now be so regulated that the gas and steam evolved never drive out more than half the liquid in *C*: otherwise there is danger of gas-bubbles entering the tubes *d* and *e* and thus escaping.

After heating for about twenty minutes, the flame under *A* is removed. In a few minutes the steam in *A* and *C* condenses, and water passes from *B* toward *C* and *A*. If a gas-bubble is observed in *A*, the flask *A* must again be heated and cooled in the manner just described. The operation is ended when the hot liquid flows back and completely fills *A*. The rubber tube *g* is then connected with a small tube which is filled with water or mercury, and the gas standing over the hot liquid in *C* is driven over into a eudiometer, gas burette, or gasometer by blowing into the tube *x* and opening the pinchcock *g*.

F. Hoppe-Seyler¹ has devised a somewhat more complicated apparatus for extracting the dissolved gases from the waters of springs and rivers. It is a modification of the method proposed by Bunsen and Dittmar. The apparatus shown in Fig. 16 varies slightly from that suggested by Hoppe-Seyler in that a gas burette *D* (see page 91) is used as the collecting vessel and air-pump. Any other burette with a two-way stopcock may,

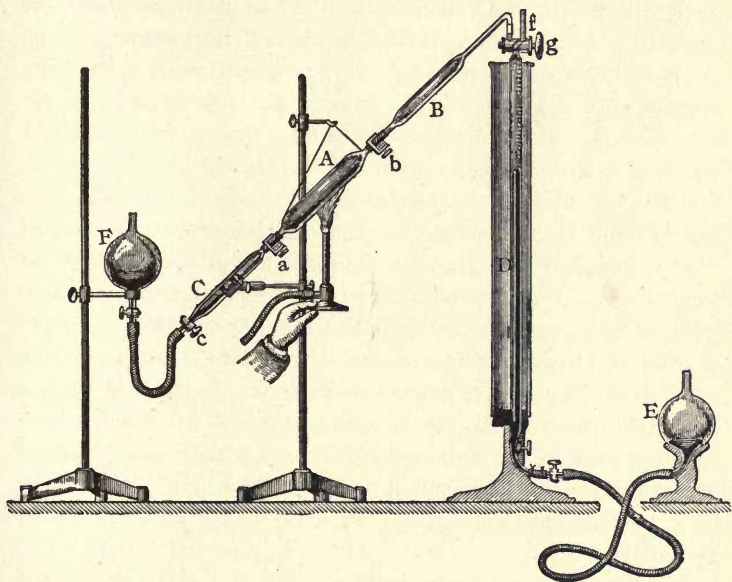


FIG. 16

of course, be employed in place of the burette here figured. The apparatus consists of the gas burette *D* filled with mercury, the glass tubes, *A*, *B*, and *C*, and the level-bulb *F*. The tubes *A*, *B*, and *C* are joined together with pieces of rubber tubing. Screw pinchcocks are placed at *a* and *b*. To extract the dissolved gases from a sample of water, a bent glass tube is inserted at *b* and the tubes *A* and *C* are filled with mercury by raising the

¹ *Zeitschr. f. analyt. Chem.*, 31 (1892), 367.

level-bulb *F*, the mercury being allowed to rise until it reaches the tube which has been inserted at *b*. The glass tube is then introduced into the vessel that contains the water to be examined, and by lowering the level-bulb *F* water is drawn into the apparatus until the tube *A* is completely filled with it. The bent tube is then removed from *b*, *B* is inserted in its place, and the pinchcock at *b* is closed. The two-way stopcock of the burette is now turned so that the burette communicates with the exit tube *f*. The air in the burette is driven out by raising the level-bulb *E*, and the stopcock *g* is then turned so that the burette communicates with the tube *B*. Upon lowering the level-bulb as far as possible the burette may now be made to function as a mercury air-pump and the air which is in *B* can be drawn over into *D*. Upon closing the stopcock *g*, raising the bulb *E*, and then turning *G* so that the burette communicates with *f*, the air which has been drawn out of *B* may be expelled from the burette. This operation is then repeated until no more bubbles of gas appear. When the tube *B* has thus been exhausted of air, the cocks *a*, *b*, and *c* are opened, and the water in the apparatus is brought to boiling by heating the tubes *A* and *C* directly with the Bunsen burner. The escape of the gas into the vacuum of *B* begins at once. After about five minutes, the water in *A* is brought nearly to the height of the pinchcock *b* by raising or lowering the level-bulb *F*. *b* is then closed and the gas in *B* is pumped out by raising and lowering the level-bulb *E* in the manner above described. *f* is connected by means of a bent capillary tube with a second gas burette or gas pipette, and the gas which has been drawn over into *D* from *B* is transferred to the second gas holder by turning *g* so that *D* communicates with *f*. The pinchcock *b* is then opened, the water in *A* is again brought to boiling, and the gas set free by this second treatment is added to the portion first obtained. By repeating the process three times it is easily possible to completely extract all of the absorbed gases with the exception of carbon dioxide. This latter gas is so persistently retained

by the water that according to the experiments of Jacobsen it is impossible to entirely remove it. Pettersson has shown that even after strongly acidifying the water with sulphuric acid the carbon dioxide cannot completely be driven out by boiling.

Collection of Gases from Reactions in Sealed Tubes. — Gases are set free in many chemical reactions that take place in sealed tubes. If one wishes to examine these gases, Bunsen directs ¹ that when the tube is fused together, it be drawn out to a fine tip about 2 mm. wide and 50 mm. long. To collect the gases given off, a mark is made at *a* (Fig. 17), with a sharp file, and the tip is connected with a capillary glass tube by means of a short piece of rubber tubing.

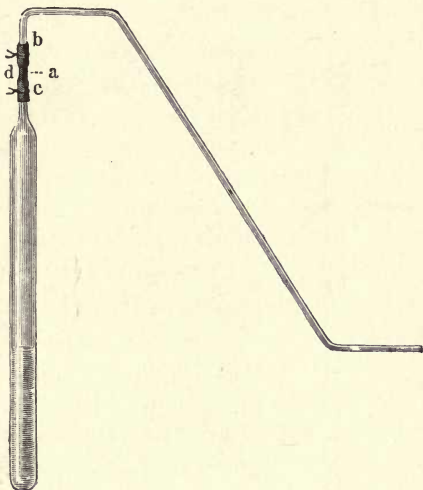


FIG. 17.

For safety's sake wire ligatures are put on at *b* and *c*. On breaking the tube inside the rubber at *a*, the gas passes through the delivery tube and can be collected in any desired receiver. If very strong pressure in the tube is to be expected, the rubber connection is surrounded with a strip of linen, and the tube itself is wrapped in a cloth. A third ligature put on at *d* makes it possible to stop the escape of gas at any time, the rubber forming with the broken-off glass tube a Bunsen rubber valve.

Extraction of Gases from Minerals. — To extract the gases

¹ Bunsen, *Gasometrische Methoden*, 2d ed., p. 10.

that may be present in minerals or rocks, Ramsay and Travers¹ recommend that the mineral first be reduced to a fine powder and be then mixed with double its weight of primary potassium sulphate. The mixture is placed in a hard-glass tube which is connected with an air-pump. After the tube has been exhausted it is heated to redness with a large Bunsen burner. The escaping gases are pumped out and are collected in a small tube

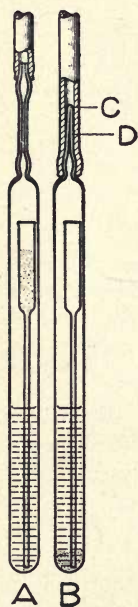


FIG. 19

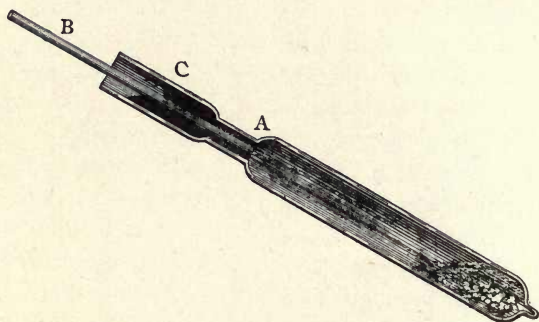


FIG. 18

that contains a small amount of a solution of potassium hydroxide. In order to exclude the possibility of leakage, the tube is joined to the air-pump in the manner shown in Fig. 18. As may be seen from the drawing, the large tube is drawn out at A, a piece of rubber tubing is placed over the end of the small tube B, and after it has been inserted in the contraction at A, the joint is covered with mercury standing in the wide portion C.

In most cases the gases that are present in the mineral are driven out by heating the substance alone without the addition of primary potassium sulphate.

To collect the gases that are set free when minerals are heated in sealed tubes with sulphuric acid Travers² uses the tube shown

¹ *Proc. Royal Soc., London*, 60 (1896), 442.

² *Proc. Royal Soc.*, 64 (1898), 132.

in Fig. 19. Sulphuric acid is first poured into the tube and the weighed sample of the finely powdered mineral is placed in a short tube that has a rod fused to the bottom of it to hold this sample tube above the surface of the acid. This tube is slipped into the large tube in the position shown in the figure, and the upper end of the outer tube is then drawn out, is connected with a mercury air-pump by means of a rubber tube, and is exhausted

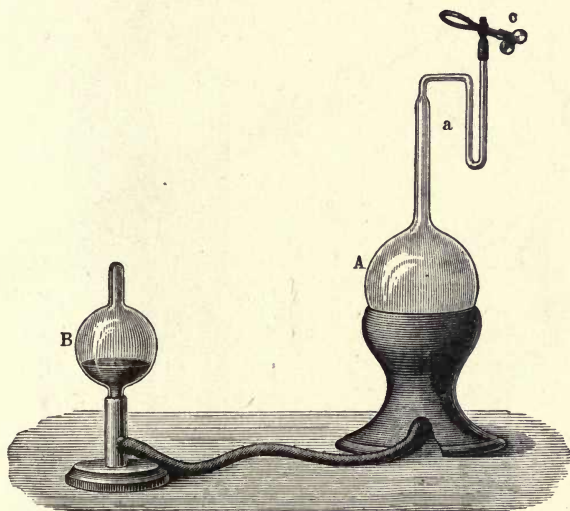


FIG. 20

and sealed by fusion at *C*. After the contents of the tube has been heated for a length of time sufficient to completely decompose the mineral the tip of the tube is marked with a file at *D*, and the tube is again attached to the pump by a piece of rubber tubing. After the air in the connecting tube has been pumped out, the tip *C* is broken off inside the rubber tube and the gas is drawn out by means of a mercury pump and is collected for analysis.

Gasometers.— If a sample of gas is to be collected and kept for analysis for a considerable length of time, the portions of

the gas taken for analysis must be displaced with mercury. Water may not be used for this purpose because its solvent power for gases would cause change in the composition of the gas mixture. A small gasometer that is suitable for prolonged storage of a gas sample is shown in Fig. 20. The large glass bulb *A* serves to hold the gas. At the top it carries the bent

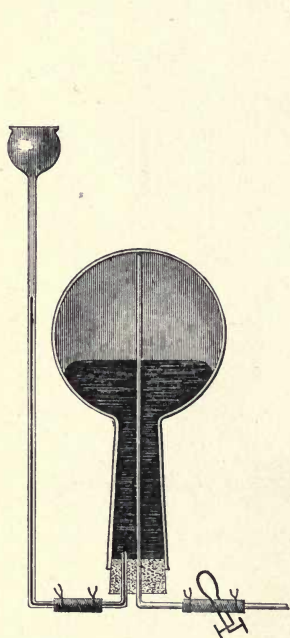


FIG. 21

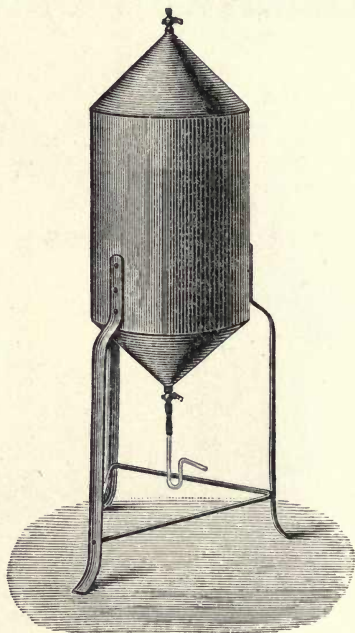


FIG. 22

capillary tube *a*, and at the bottom it is joined to the level-bulb *B* by a rubber tube. The capillary is closed by a rubber tube and pinchcock. The apparatus is first filled with mercury. By lowering or raising the level-bulb, gas can be drawn in or driven out as desired. If gases are to be kept for some time, the capillary tube *a* is filled with mercury by means of a little pipette inserted at *c*. This closes the bulb perfectly.

A convenient gasometer may easily be constructed from a round-bottomed flask fitted with a two-hole rubber stopper and bent glass tubes in the manner shown in Fig. 21. The thistle tube may be replaced by a level-bulb and rubber tube (see Fig. 20).

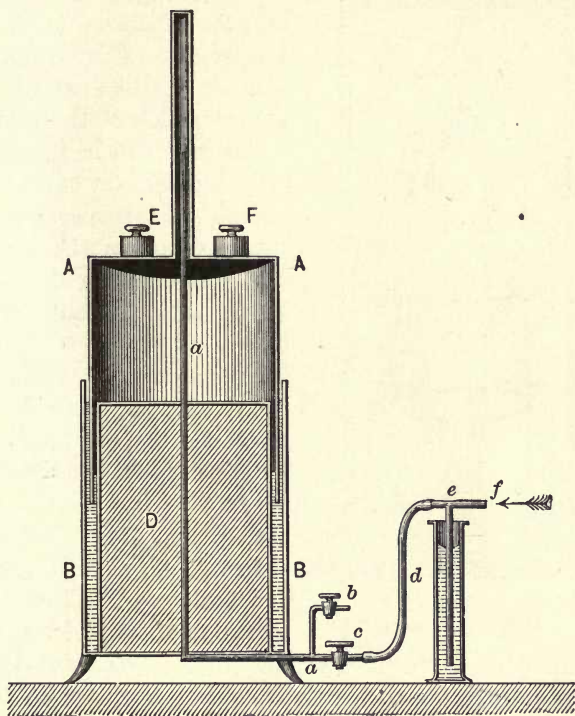


FIG. 23

For the collection and storage of large samples of gas, gasometers made of sheet zinc, of sheet iron or galvanized iron, or of glass may be employed. The form shown in Fig. 22 may also be used to aspirate the gas into the container. The large

gasometers that ordinarily are used in laboratories are not well adapted to the storage of gas samples for analysis because of the solvent action of water upon the constituents of the gas mixture. This defect may partially be remedied by using a concentrated solution of sodium chloride or of magnesium chloride as

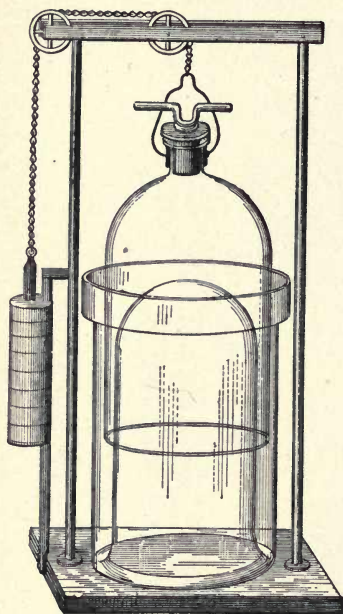


FIG. 24

confining liquid or by bringing a layer of paraffin oil upon the surface of the water.¹ The solvent action of the confining liquid may also be lessened by using a gasometer of such form as will give small surface of contact between the gas mixture and confining liquid. An instrument of this type is shown in Fig. 23.

The gasometer consists of the bell *A* which dips into the cylindrical ring-shaped space *B*, this latter being filled with a solution of magnesium chloride. The shaded part *D* is a hollow cylinder closed at both the top and bottom. The iron tube *a* serves as a guide for the bell and should therefore be made quite wide. The gasometer is filled by introducing the gas in question through *f*. A branch tube at *e* extends downward into a glass cylinder filled with water and serves the double purpose of enabling the operator to observe the pressure of the gas and to drive out any air in the tubes through this branch. The weights *E* and *F* make it possible to regulate at will the pressure in the gasometer.

¹ See Voigt, *Chemiker-Zeitung*, 32 (1908), 1082, and Reinhardt, *Chemiker-Zeitung*, 33 (1909), 206.

When the gasometer has been filled, the rubber tube *d* is removed from *c*. The gas can then be drawn off through either the stopcock *b* or *c*.

A glass gasometer constructed on the same principle as the foregoing is shown in Fig. 24.

CHAPTER II

THE MEASUREMENT OF LARGE SAMPLES OF GAS

When a gas is present in a gas mixture in only very small amounts, it is usually determined by drawing or forcing a large sample of the gas mixture through a suitable absorption apparatus, and ascertaining the amount of the absorbed constituent by gravimetric or volumetric means. It is evident that under such circumstances the large size of the gas sample obviates the necessity of very accurately determining its volume (see page 122).

An arrangement of apparatus that is suitable for the approximate measurement of large gas volumes, and that can easily be put together from stock apparatus in the laboratory, is shown in Fig. 25. The large bottle *B* is filled with water, and the stopper carrying the inlet tube and the siphon tube *D* is then inserted in the neck of the bottle. *D* is filled with water by blowing into the inlet tube, and the screw pinchcock *E* is then closed. *B* is now connected with the absorption apparatus *A* through which the sample is to be drawn, and the pinchcock *E* is opened. When the first bubble of gas passes through the absorbent, a measuring cylinder *C* is placed under the end of the siphon tube, and the water drawn over from the bottle *B* is thus measured. After the operation is complete, the volume of gas represented by the water that has been measured off in the cylinder *C* is reduced to standard conditions and the percentage of the absorbed constituent in the original gas volume is then calculated.

Gas Meter.—A more convenient but more expensive apparatus for measuring large gas volumes is an Experimental Gas Meter¹ of the type shown in Fig. 26. The meter is a “wet”

¹ These meters may be obtained from S. Elster, Berlin.

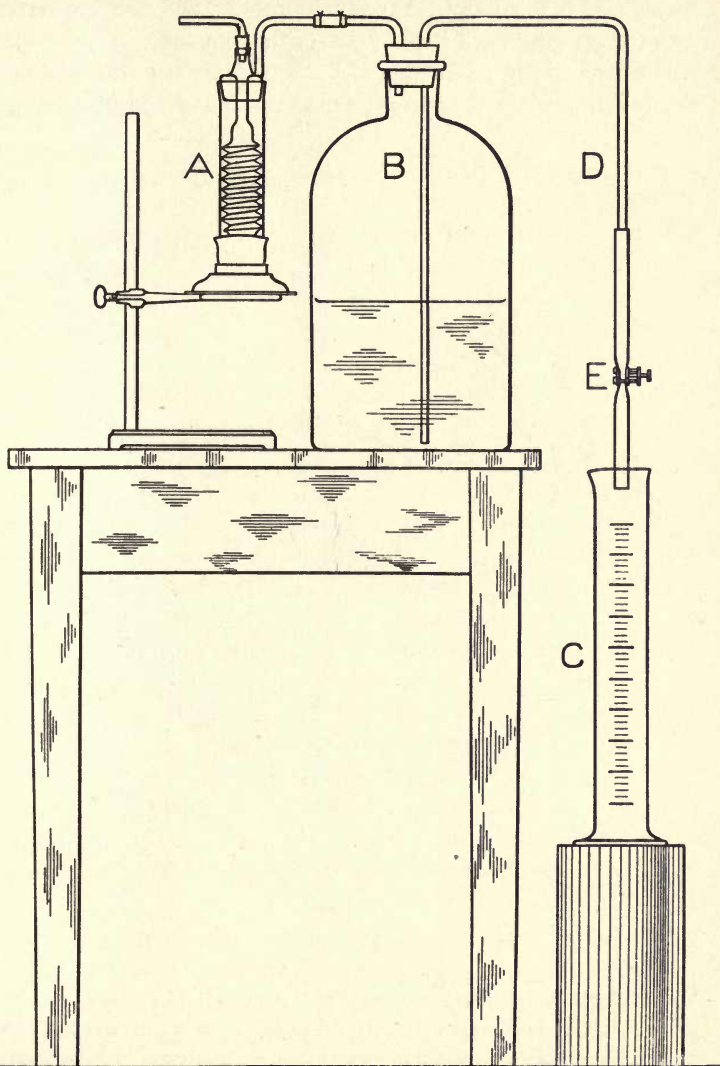


FIG. 25

meter and is filled by removing the cap *M* and pouring water into the opening until it flows out of the opening *C* in the lower part of the meter. The caps of both openings are then screwed firmly into place. The gas enters the meter at *F*, passes through

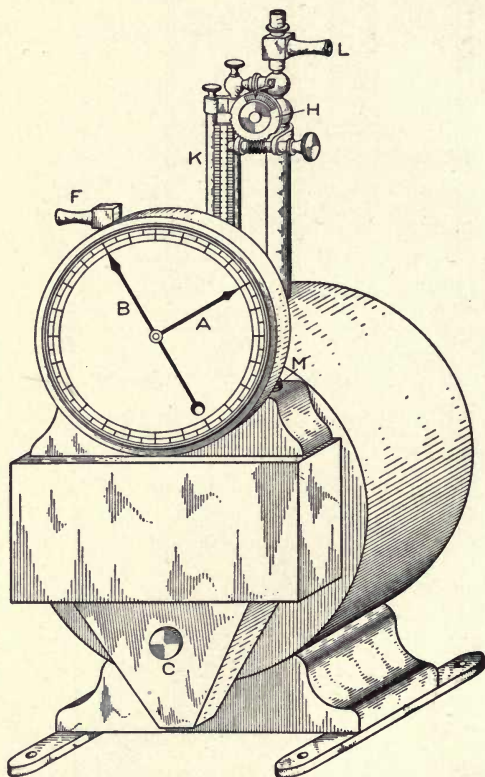


FIG. 26

the measuring drums, and escapes through the tube *L*. Its speed of flow may be delicately adjusted by a micrometer screw that turns the dial *H*. The manometer *K* shows the pressure of the gas. The dial of the meter is provided with two hands.

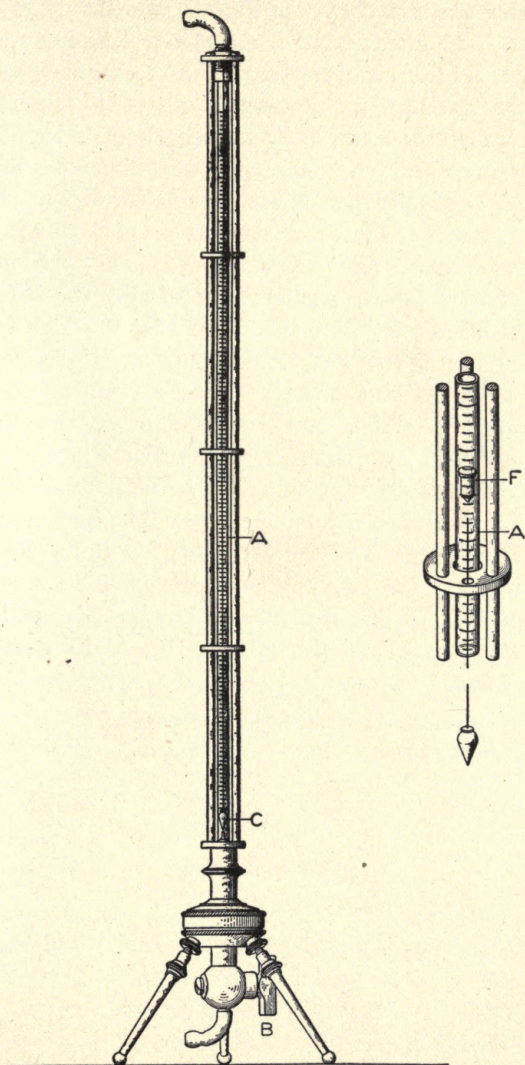


FIG. 27

The shorter one *A* records the liters of gas that pass through the meter. The longer hand *B* makes one complete revolution for every three liters and is of use in the measurement of small gas volumes and also in the measurement of the amount of gas passing through the meter in a relatively short period of time.

The Rotameter. — A unique and useful device for measuring the volume of gas per hour that is flowing through a tube is the rotameter¹ shown in Fig. 27. It consists of a glass tube *A* through which the gas passes from below upward. The speed of flow of the gas current can be regulated by turning the stopcock *B*. Inside the glass tube there is a little float *F* which is carried upward by the flowing gas, and at the same time set in rapid rotation about its vertical axis. The float will rise or sink in the glass tube according to the amount of gas that is passing through the tube, and the height of the float, which is measured by a scale attached to the tube, shows the number of liters of gas flowing through the tube per hour. The scale on the tube is an arbitrary one, and the instrument is calibrated for one particular gas. The rotameter is made in different sizes, the maximum flow of gas through the smallest size being about 200 liters per hour, and through the largest size about 30,000 liters per hour.

¹ This instrument may be obtained from the Rotawerke, Aachen, Germany.

CHAPTER III

THE MEASUREMENT OF GASES

The quantity of a gas may be determined either by measuring its volume, or by ascertaining its weight, or by causing it to enter into chemical reactions that render possible its determination by indirect gravimetric or volumetric methods. Because of the comparatively low densities of gases, the first method is usually most accurate as well as most convenient. In fact in gas analytic work the determination of the amount of a gas by direct measurement of its weight is but rarely employed.

THE REDUCTION OF THE VOLUME OF A GAS TO STANDARD CONDITIONS

The volume of a gas is affected by changes of pressure and of temperature.

The Law of Boyle. — The effect of change of pressure is expressed in the Law of Boyle: *Provided the temperature remains constant, the volume of a gas is inversely proportional to the pressure.*

$$v_0:v = p:p_0, \text{ or}$$

$$v_0p_0 = vp. \quad (1)$$

The Law of Charles. — If a gas at 0° C. be warmed to 1° C. (the pressure remaining constant) it will expand $\frac{1}{273}$ of the volume that it occupied at 0° . If the temperature of the gas be raised from 0° to 273° , its volume will double. Similarly, if a gas be cooled below 0° , its volume will decrease $\frac{1}{273}$ of its volume at 0° for each degree of fall of temperature below 0° . These facts are briefly stated in the Law of Charles: *Provided*

the pressure remains constant, the volume of a gas will change $\frac{1}{273}$ or 0.00367 of its volume at 0° for each degree of change of temperature. If v_0 represent the volume of the gas at 0° and v the volume at a temperature t and $\alpha = \frac{1}{273}$.

$$v = v_0 (1 + \alpha t), \text{ or}$$

$$v_0 = \frac{v}{1 + \alpha t}. \quad (2)$$

Similarly, the volume v_1 of the gas at a temperature t_1 would from (2) be

$$v_1 = v_0 (1 + \alpha t_1), \text{ or}$$

$$v_0 = \frac{v_1}{1 + \alpha t_1} \quad \text{Consequently,}$$

$$\frac{v}{1 + \alpha t} = \frac{v_1}{1 + \alpha t_1}. \quad (3)$$

Furthermore, if the volume of a gas remains constant, its pressure will change $\frac{1}{273}$ or 0.00367 of its pressure at 0° for each degree of change in temperature.

$$p = p_0 (1 + \alpha t) \quad \text{or}$$

$$p_0 = \frac{p}{1 + \alpha t}.$$

$$p_1 = p_0 (1 + \alpha t_1) \quad \text{or}$$

$$p_0 = \frac{p_1}{1 + \alpha t_1}.$$

$$\frac{p}{1 + \alpha t} = \frac{p_1}{1 + \alpha t_1}. \quad (4)$$

Since the effect of change of temperature is represented by the same formula whether pressure or volume is under con-

sideration, by combining (3) and (4) there is obtained the expression

$$\frac{vp}{1 + \alpha t} = \frac{v_1 p_1}{1 + \alpha t_1} \quad (5)$$

In stating the volume of a gas it is agreed among scientists to express it in terms of the volume that the gas would occupy under certain arbitrary conditions (standard conditions) namely—at a temperature of 0°C. and under a pressure of 760 mm. of mercury. To reduce an observed gas volume to the volume that it would occupy under standard conditions we may employ the formula (5). Since

$$\frac{vp}{1 + \alpha t} = \frac{v_1 p_1}{1 + \alpha t_1} \text{ it must also be true that}$$

$$\frac{v_0 p_0}{1 + \alpha t_0} = \frac{vp}{1 + \alpha t} \quad \text{If now } p_0 = 760 \text{ and } t_0 = 0^\circ \text{C.}$$

then since $\alpha = 0.00367$

$$v_0 760 = \frac{vp}{1 + 0.00367t} \quad \text{or}$$

$$v_0 = v \frac{p}{760(1 + 0.00367t)} \quad (6) \text{ in which } v_0$$

is the volume under standard conditions, v the observed volume, p the observed pressure expressed in millimeters of mercury and t the observed temperature.

By means of the above formula (6) a gas volume may correctly be reduced to standard conditions provided the gas, when measured, contains no water vapor. If, however, water vapor is present, a correction must be introduced. Every liquid tends to change to the gaseous state and the vapor of the liquid exerts a gas pressure which is termed the *vapor pressure* of the liquid. This vapor pressure is dependent upon the temper-

ature and upon the nature of the liquid, but it is not affected by the pressure of other gases, nor by the amount of the liquid that is present. If a closed space is filled with a mixture of gases, each gas will exert a definite pressure which is the same whether it exists alone in the space or whether other gases are present. The total pressure of the gas mixture is the sum of the partial pressures of the various gases. If now a gas volume that contains water vapor is measured at atmospheric pressure, the partial pressure of the dry gas will equal the barometric pressure less the pressure of the water vapor in the gas. If the gas is not "saturated" with water vapor, the partial pressure of the latter is difficult to determine. But when a gas is measured over water, or over mercury upon which stands a small amount of water, the space is saturated with water vapor, and since the maximum pressure of water vapor at various temperatures is known (see table on p. 411) the pressure of the dry gas can easily be ascertained by noting the temperature of the gas and subtracting from the observed barometric pressure the pressure of water vapor at the observed temperature. Representing the pressure of the water vapor by m , and inserting this correction in formula (6), we obtain

$$v_0 = v \frac{p - m}{760 (1 + 0.00367t)} \quad (7)$$

Inasmuch as the vapor pressures of liquids vary with the nature of the liquids, it is apparent that if a gas is measured over a liquid other than pure water the correction to be introduced for the vapor pressure of the liquid will not be the same as for that of pure water. For this reason those forms of apparatus in which gas volumes are measured over concentrated solutions of various absorbents will not yield accurate results unless the vapor pressure of each solution is known and taken into account. To avoid error from this source it is now customary, in the better types of apparatus, to pass the gas mixture from a measuring burette into a separate apparatus containing the absorbent,

and to then draw the gas back into the burette where it comes into contact with water before being again measured. In this manner the space occupied by the gas is always saturated with water vapor when the volume of the gas is measured.

When a gas is measured over dry mercury, the vapor pressure of the mercury is so small as to be negligible unless the gas is measured at a temperature considerably above 40° .

THE LUNGE GAS VOLUMETER

To facilitate work with the nitrometer (p. 397) Lunge has devised an instrument, the gas volumeter, with the aid of which a volume of gas in the measuring tube of the apparatus may quickly be brought to the volume that it would occupy under standard conditions. This does away with the usual calculations and effects a considerable saving of time.

The instrument, Fig. 28, consists of a gas burette *A*, a reduction tube *B*, and a level-tube *C*, which are connected at the lower ends by pieces of enamelled rubber tubing and the T tube *D*.

The gas burette *A* has a

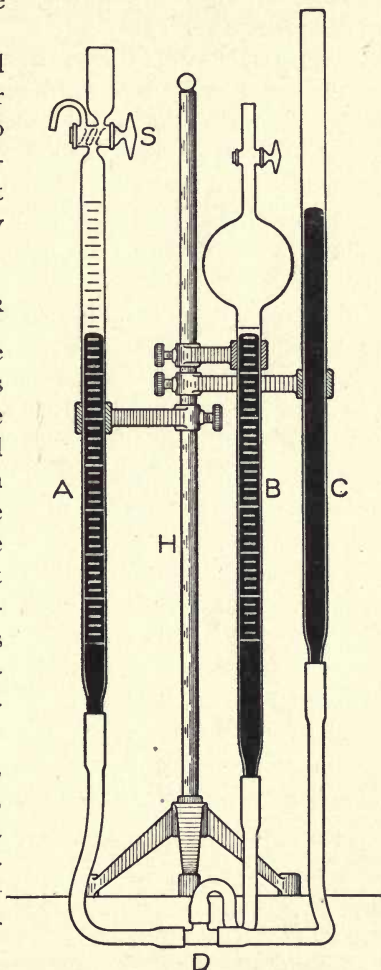


FIG. 28

capacity of somewhat more than 100 cc. and is calibrated from the stopcock downward in 100 cc. divided into $\frac{1}{5}$ cc. At its upper end is a two-way stopcock *S*. The upper tubes of the stopcock are capillary and one of them is bent over and downward as shown in the figure.

The reduction tube *B* is provided with a single bore stopcock at the upper end. Below the stopcock it is widened into a bulb. From the stopcock to a mark on the tube somewhat below the bulb the tube holds exactly 100 cc. From the 100 cc. mark downward the tube is calibrated to about 140 cc. in $\frac{1}{10}$ cc.

The level-tube *C* is a plain tube open at the top. The three tubes are fastened in clamps that are attached to the iron stand *H*.

To prepare the apparatus for use it is first necessary to inclose in the reduction tube a volume of moist air that, under standard conditions and in the dry state, would have a volume of exactly 100 cc. This is accomplished as follows:—

The apparatus is filled with clean mercury and somewhat more than 100 cc. of air is then drawn into the reduction tube *B* by opening the stopcock of the tube and lowering the level-tube *C*. A drop of water is next drawn into the bulb of *B* through the stopcock to insure that the space above the mercury in the reduction tube is saturated with water vapor. A thermometer is hung close to the apparatus, and after the apparatus has come to the temperature of the room, the thermometer and barometer are carefully read.

The volume that 100 cc. of air, under standard conditions, would occupy under the observed temperature and pressure is now calculated from the formula

$$v = v_0 \frac{760(1 + .00367t)}{p - m}$$

which is derived directly from (7) on p. 36, and in which $v_0 = 100$ cc.

The stopcock of the reduction tube is now opened, and the

level-tube is raised or lowered until the mercury in *B* stands exactly at the volume calculated for *v*. The stopcock of *B* is then closed. There is thus inclosed in the reduction tube a volume of air that will occupy exactly 100 cc. when measured under standard conditions.

If now a gas is brought into the burette *A*, the volume that it would occupy under standard conditions may rapidly be ascertained in the following manner.

The level-tube *C* is raised or lowered until the mercury in the reduction tube *B* stands close to the 100 cc. mark, and *C* is then clamped firmly in that position. The burette *A* is now raised or lowered until the mercury in it stands at the same height as that in the reduction tube and it is then clamped in position. This adjustment will usually cause the mercury to move up or down from the 100 cc. mark in *B*. It is brought back to the mark by again changing the height of the level-tube and the burette is again raised or lowered until the mercury in it and in *B* are at the same level. These adjustments are repeated until, with the mercury in *A* and *B* at the same height, the mercury in the reduction tube *B* stands exactly at the 100 cc. mark.

Since the pressure upon the air in *B* suffices to bring it, at the now prevailing temperature, to the volume that it would occupy under standard conditions, it follows that the gas in the burette *A*¹, if at the same temperature as the air in *B*, will also be brought to the volume that it would occupy under standard conditions, and consequently its corrected volume may be directly read off.

The Lunge gas volumeter is open to criticism because the burette and the reduction tube stand free in the air and for that reason are subject to sudden and different changes of temperature. This may cause appreciable error since a difference of only 1° C. would mean a variation of 0.3 per cent in the gas

¹ The space above the mercury in *A* must be of course saturated with water vapor as is the space in *B*.

volume. For this reason the apparatus will give dependable results only when it stands in a room of uniform temperature and free from drafts, and when in the manipulation great care is exercised to avoid the uneven warming of the tubes by heat from the hands or from the body of the operator.

THE BODLÄNDER GAS BAROSCOPE

Bodländer has devised¹ an ingenious instrument with the aid of which the *weight* of the gas in the measuring burette may be calculated in very simple manner from its pressure.

A volume of gas v that is measured at t° and under a pressure of p mm. may be reduced to the volume that it would occupy under standard conditions v_0 according to the equation

$$v_0 = \frac{v \times p \times 273}{760 (273 + t)}.$$

Since the weight of a cubic centimeter of a gas of the molecular weight M is equal to $0.0446725 \times M$ mg., the weight G of v cc. of the gas

$$G = \frac{v \times p \times 273 \times 0.0446725 \times M}{760 (273 + t)} \text{ mg.} \quad (1)$$

If in all of the measurements the volume is adjusted so that

$$v = \frac{760 (273 + t)}{273 \times 0.0446725 \times 100} \text{ cc.} \quad (2)$$

then equation (1) may be reduced to the simple form

$$G = \frac{p \times M}{100} \text{ mg} \quad (3)$$

If now an apparatus is so constructed and calibrated that the volume of a gas corresponding to equation (2) at a prevailing temperature of t° may easily be ascertained, then the weight

¹*Z. f. angew. Chem.*, 1894, 425.

of the gas in milligrams may be determined by bringing the gas to this volume, ascertaining the pressure exerted by the gas, and multiplying this pressure, expressed in decimeters, by the molecular weight of the gas.

The instrument that Bodländer devised for this style of analysis is termed by him a gas baroscope. The essential parts of the apparatus are shown in Fig. 29. The measuring tube consists of the bulb *A* which is about 7 cm. in diameter, and a tube *B* on which is marked a scale running from zero at the top to 30 near the bottom, each division being divided into fifths. *A* and *B* are surrounded by a water mantle. The upper end of the tube is closed by the two-way stopcock *S* that ends in the capillaries *C* and *D*. The capacity of the measuring tube from the lower side of the stopcock to the mark zero on the tube *B* is the volume at 0° calculated from equation (2) when $t = 0$. The volume down to division one is that at 1° calculated for $t = 1$, and so on.

The lower end of the measuring tube *B* is connected by a piece of enamelled rubber tubing with the level-bulb *L* which is provided with

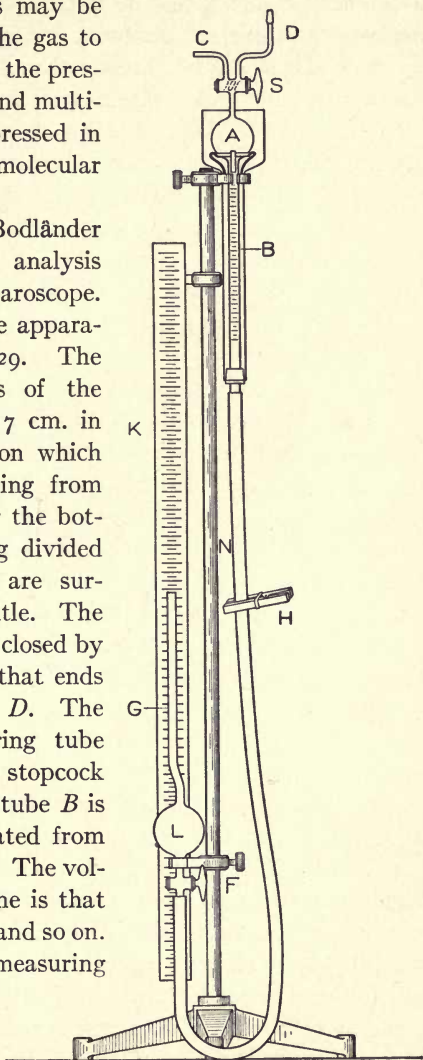


FIG. 29

a stopcock *F* and a bent tube *G* that is about 12 mm. internal diameter and projects about 27 cm. above the bulb. The contents of *L* is somewhat greater than that of the bulb *A*. The measuring tube and the level-bulb are fastened by clamps to an iron stand *M* that is about 1.2 meter high. The level-bulb *L* and the clamp that carries it may be slid up and down upon the rod in such manner that the tube *G* of the bulb lies close to the front of a meter scale *K* that is divided into millimeters and hangs in a perpendicular position from a clamp attached near the upper end of the rod.

The measurements with the gas baroscope are made in the following manner. The instrument is filled with clean mercury. The air in the bulb *A* is completely driven out through the capillary tube *C* by opening the stopcock *S* and raising the level-bulb. The capillary tube *D* is then connected with the evolution apparatus or the container that holds the gas that is to be measured and the gas is drawn into the bulb *A* by turning the stopcock *S* to proper position and lowering the level-bulb *L*. *S* is then closed and the level-bulb *L* is lowered until the gas in *A* and *B* is expanded to such a volume that the mercury in *B* stands at the mark on the scale that corresponds to the prevailing temperature. The sharp adjustment of the mercury to this mark is accomplished by lowering *L* until the mercury in *B* stands somewhat below the mark, and then turning down the clamp *H* upon the rubber tube until the mercury is brought exactly to the proper height. The apparatus must contain such an amount of mercury that this will now stand in the tube *G* above the level-bulb. *G* itself stands close to the scale *K*, but should not be allowed to touch the scale and thus push it out of its perpendicular position. The height of the mercury in *G* is now carefully read off on the scale *K* with the naked eye. This reading can be made to an accuracy of about one-tenth mm. but the readings are of course more accurate if made with a cathetometer.

To ascertain the pressure exerted by the gas in *A* a second

reading is necessary. The gas is first driven out of *A* through the capillary tube *C* by opening *S* and raising the level-bulb. *S* is then closed and *L* is lowered until the mercury in the tube *B* stands at exactly the same position as before. The height of the mercury in *G* is then read off upon the scale, and the difference between this reading and the first reading on the scale expressed in decimeters and multiplied by the molecular weight of the gas gives the weight of the gas in milligrams.

If a mixture of gases has first been introduced into the measuring tube and the weight of a constituent gas is desired, the pressure of the gas mixture is first ascertained in the manner above described, the capillary tube *C* is then connected with a suitable absorption pipette for the removal of the constituent in question, the gas mixture is driven over into this pipette and is then drawn back into *A*. The mercury in *B* is now again brought to the original mark, the pressure is read, and from the difference in pressure, the weight of the absorbed constituent is calculated.

If the gas that is being measured is saturated with moisture, a drop or two of water should be introduced into *A* upon the mercury before the final measurement of the pressure, after the removal of the gas, is made. No correction for the tension of water vapor is then necessary.

CHAPTER IV

THE DETERMINATION OF THE SPECIFIC GRAVITY OF A GAS

The determination of the specific gravity of a gas may conveniently be made by Bunsen's method ¹ of measuring the time of escape of the gas.

This method is based upon the fact that the specific gravities of two gases escaping through small openings in thin plates bear nearly the same ratio to each other as the squares of their times of escape. If a gas of the specific gravity s has a time of flow t , and another gas of a specific gravity s_1 has a time of flow t_1 , the relation between the time of escape and the specific gravity is given by the equation —

$$\frac{s_1}{s} = \frac{t_1^2}{t^2}.$$

If s or the specific gravity of one of the gases be regarded as 1, the specific gravity of the other gas is found by the formula —

$$s_1 = \frac{t_1^2}{t^2}.$$

Figure 30 shows the apparatus used for this determination. A glass tube of about 70 cc. capacity is luted into the iron cap A . This cap is fitted with a three-way stopcock by means of which the inside of the glass tube can be brought into communication with either the tube B through which the gases are introduced, or the small opening in C . This opening is made in a platinum plate, which is about as thick as tin foil, and is luted in position. To obtain an opening as small as needed, the

¹ Bunsen, *Gasometrische Methoden*, 2d ed., p. 184.

platinum foil is pierced with a fine sewing needle, and is hammered with a polished hammer upon a polished anvil until the opening can no longer be seen with the naked eye, and is visible only when the plate is held between the eye and a bright flame. The plate thus perforated is cut out in the form of a small circular disk, the opening being at the center.

In order that the gases to be examined may always escape through the opening *C* under the same conditions as regards pressure, there is placed in *A* a float *bb*. This float should be as light as possible, and for this reason it is best made from a very thin-walled glass tube. The float has at β a little button of black glass from which projects a small, white glass point.

Two fine threads of black glass, β_1 and β_2 , are fused around the lower part of the stem of the float. These two threads, together with the black glass button at the top, serve as marks.

If the tube containing the gas be pushed down so far into the mercury that a mark on the glass is tangent to the outer mercury surface, then the float which is inside the tube is no longer visible through the telescope.

If now the stopcock be opened and the gas allowed to escape through the opening in the platinum plate, the float rises, being carried up upon the surface of the mercury in the tube. If the level of the external mercury be observed through the telescope, the white glass tip of the float soon comes into the field, and informs the observer that the black button β will shortly appear.

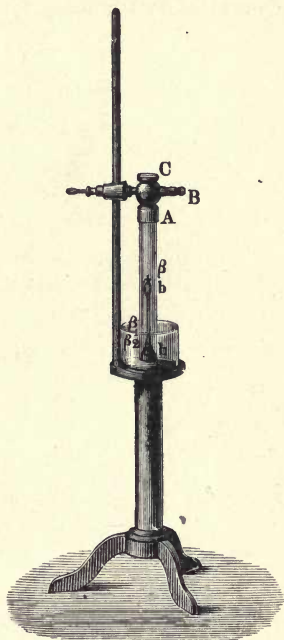


FIG. 30

When this comes in sight the time is taken, the end of the timing being at that moment at which the mark β_2 comes into the field of the telescope; the near approach of β_2 is here shown by the appearance of β_1 .

From these observations is obtained the time of escape of a column of gas which, measured from β , has the length shown

by the marks $\beta\beta_2$ on the float; moreover, the gases escape under the same differences of pressure in all of the experiments. The times taken by the different gases to escape through the fine opening in *C* give, when squared, the ratios of the specific gravities of the gases.

The gases must be dried, and the mercury must be pure and dry. An advantage of the Bunsen apparatus is that a determination can be made with a very small quantity of the gas.

Schilling has given the apparatus a very practical form for the examination of illuminating gas, where large amounts of the gas are usually available.

A (Fig. 31) is a glass tube of 40 mm. internal diameter and about 450 mm. long. The upper end is luted into a brass cover *C* into which is inserted the tube *B*

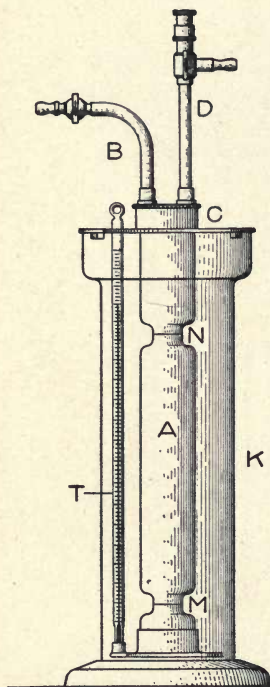


FIG. 31

through which the gas is led in. The gas escapes through a perforated platinum disk in the upper end of the tube *D*. A thermometer *T* is immersed in the water of the cylinder *K*. The inner cylinder has two marks, *M* and *N*. The apparatus is filled with water.

To determine the specific gravity of an illuminating gas with this apparatus, the tube is first filled with air, and the time of escape of the air, under the prevailing temperature and pressure, is noted. The last trace of air is then removed by repeatedly drawing in and driving out the gas to be examined, and the time of escape of the illuminating gas is then observed. The squares of the values are directly proportional to the specific gravities of the gases. Since the specific gravity of air is usually taken as 1, the calculation is very simple.

The Schilling apparatus is open to objection because of the inconvenience in filling the inner cylinder with the gas under examination. Moreover, the marks are so far apart as to render the reading of them somewhat awkward. These drawbacks are avoided in the modification of the apparatus devised by Pannertz,¹ who uses two glass bulbs that are connected by a piece of rubber tubing (Fig. 32). The measurements are made with the flask at the right which has an iron cap C of the same general construction as that used with the Bunsen apparatus. The two marks A and B are placed upon the narrow necks of the bulb. The flask is filled with air or with the gas mixture by first raising the level bulb and filling the measuring bulb with water and then placing the measuring

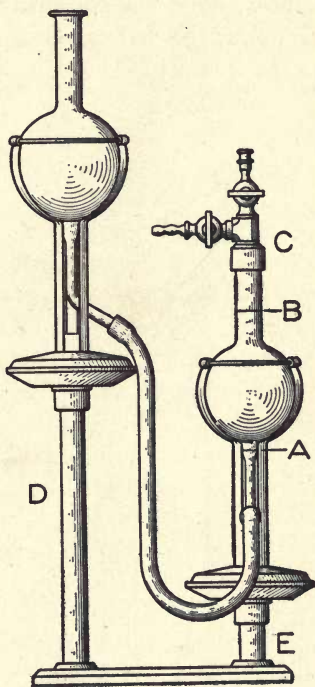


FIG. 32

¹ *J. f. Gasbeleuchtung*, 48 (1905), 901.

bulb on the stand *D* and drawing in the air or gas through the side arm of the iron cap. In measuring the time of escape of the air or gas, the measuring vessel is placed upon the stand *E* and the level bulb is placed upon the stand *D* as shown in the figure. When the apparatus is charged with the right amount of water, the water will rise above the upper mark *B* nearly to the iron cap.

CHAPTER V

ARRANGEMENT AND FITTINGS OF THE LABORATORY

The room for gas analysis should have a northern exposure and should have wide windows. The working-table should run along the outer wall so that the operator may face the window and be able to make his readings without being obliged to turn around toward the source of light. The floor should be of cement, and should slope slightly toward the middle in order that any mercury that may be spilled may easily be brought together and taken up. If the floor is of wood, it may be made mercury-tight by covering it with linoleum. The room should further be provided with gas and with running water and with a large sink. The sink should have an iron "S" trap, and the lower bend of this trap should be bored, threaded, and provided with a screw plug to permit of the easy removal of any mercury that may collect in the trap.

There should also be an ample supply of water of the temperature of the room. It is convenient to have this water piped to every working-place. This is cheaply accomplished by placing near the top of the room and above the sink a galvanized iron tank containing 100 liters or more, and running from the lower part of this tank an iron pipe that passes along the tables. The tank is easily filled through a small iron pipe which hooks over its top and reaches down into the sink, where it may be connected with the faucet by a piece of rubber tubing.

The laboratory should also contain a mercury air-pump, a barometer, accurate thermometers, and water suction-pumps at the working-tables. An electric current is necessary, and

this may be supplied either by a battery or storage cells, or the direct current from a dynamo may be utilized. A small induction coil is needed for analysis of gas mixtures by explosion. It is desirable to have narrow shelves fastened to the wall upon which to place the Hempel pipettes.

CHAPTER VI

APPARATUS FOR GAS ANALYSIS WITH WATER AS THE CONFINING LIQUID

THE HEMPEL SIMPLE GAS BURETTE (Fig. 33) ¹

This consists of two glass tubes, *A* and *B*, which are set in iron feet, *F* and *D*, and are connected by a rubber tube of 7 mm. internal diameter, 12 mm. external diameter, and about 120 cm. long. To facilitate the cleaning of the burette the rubber tube may be divided in the middle and the two ends joined by a piece of glass tubing.

Inside the feet the tubes *A* and *B* are bent at right angles and conically drawn out. The end projecting from the iron is of about 4 mm. external diameter and is somewhat corrugated, so that a rubber tube may be tightly fastened to it by wire ligatures.

The measuring tube *A* ends at the top in a capillary tube *C* of 1 mm. internal diameter, 6 mm. external diameter, and about 3 cm. long. Over this a short piece of soft rubber tubing, 3 mm. internal diameter, and 6.5 mm. external diameter, is wired on. The rubber tube is closed by a Mohr pinchcock *E* which is put on close to the end of the capillary. Originally the burette terminated in a glass stopcock, but this renders the apparatus fragile and costly. If the apparatus is properly manipulated during the analysis the rubber tube does not come in contact with more than traces of the absorbent and will remain in good condition for a considerable length of time. It should, however, be tested from time to time to see that it is tight. The pinchcock should always be taken off from the

¹ The Hempel apparatus for technical gas analysis is excellently constructed by Greiner and Friedrichs of Stützerbach in Thüringen, Germany.

rubber tube after using as this helps much to keep the latter in good condition. Notwithstanding the fact that readings cannot be made under the rubber tube, no measurable error re-

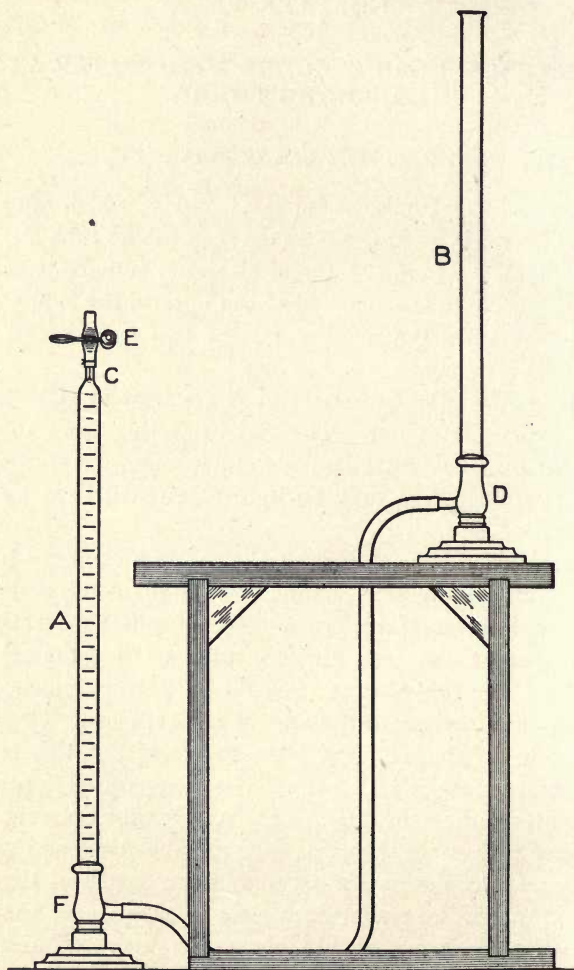


FIG. 33

sults therefrom, since the internal diameter of the glass tube *C* is very small. The differences in volume are much less than a tenth of a cubic centimeter, a variation which, in determinations not made over mercury, may be entirely disregarded. The graduated measuring tube *A* contains 100 cc., the lowest mark being slightly above the iron foot. The cubic centimeters are divided into fifths, and the numbers run both up and down. The level-tube *B* is somewhat widened at the upper end to facilitate the pouring in of the confining liquid.

In the Hempel method of gas analysis the absorbable constituents of a gas mixture are successively removed by passing the gas into a series of gas pipettes containing suitable reagents. The construction of these pipettes is such as to render it possible to bring the gases into intimate contact with the absorbents. The pipette may even be disconnected from the burette and vigorously shaken. There must be at least as many pipettes as there are absorbable constituents in the gas mixture.

The following forms, varied to suit the nature of the different reagents, are used:

THE HEMPEL SIMPLE ABSORPTION PIPETTES

These are modifications of the Ettling gas pipette, first used by Doyère for the absorption of gases, and they are filled with such absorbing liquids as are not affected by the air.

The Hempel Simple Absorption Pipette for Liquid Reagents

It consists of two large bulbs, *a* and *b* (Fig. 34), joined by the tube *d*, and of a capillary glass tube *c* of 1 mm. internal diameter, and 6 mm. external diameter and bent as shown in the figure. The distance *h* must be greater than *g* to render it possible to inclose a gas between two columns of liquid in the pipette.

The bulb *a* holds about 100 cc., and *b* about 150 cc., so that when 100 cc. of gas is brought into *b*, sufficient space for the absorbing liquid will remain. To protect the pipette from

being broken and to facilitate its manipulation, it is fastened to a wooden or iron stand.

An iron stand is preferable to wood because its greater weight renders it more stable and because it cannot warp out of shape. An iron stand with a four-sided base is superior to one with legs only at the ends because with the latter form of base there is danger that one leg of the pipette may be pushed over the

edge of the stand (see Fig. 38) and the apparatus fall and be broken.

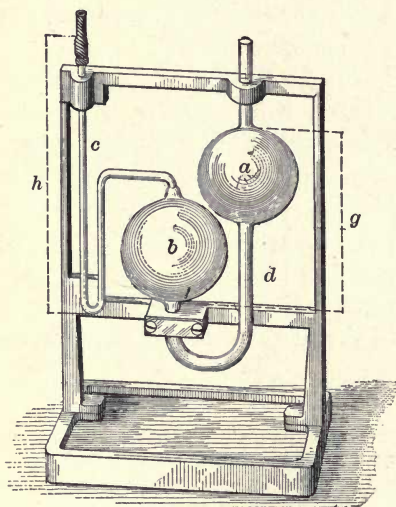


FIG. 34

The pipette is fastened in the iron standard at the three points shown in Fig. 34. The capillary tube and the tube above *a* are slipped through openings in the upper bar of the frame and the tube below *b* is set back against the lower cross-bar. The small plate that closes this lower opening is then fastened in place by screws, and the spaces between the three tubes and their iron

collars are filled with Plaster of Paris. It is well to bring the Plaster of Paris up around the lower part of *b* for the purpose of giving the bulb additional support. If the pipette is broken, the plate is unscrewed, the glass parts and the Plaster of Paris are broken out and a new pipette is slipped into place and fastened as above described. With the style of mounting here recommended, the breakage of the Hempel pipettes is very slight, and the life of the apparatus is much greater than when the pipettes are mounted on light wooden frames, or are held in place by clamps and corks as some writers have advised.

The capillary tube should project from two to three cm. above the frame. A short piece of rubber tubing is wired on the free end of the capillary.

The Hempel Simple Absorption Pipette for Solid and Liquid Reagents

The only difference between this and the simple pipette is that in place of the bulb *b* there is inserted the cylindrical part

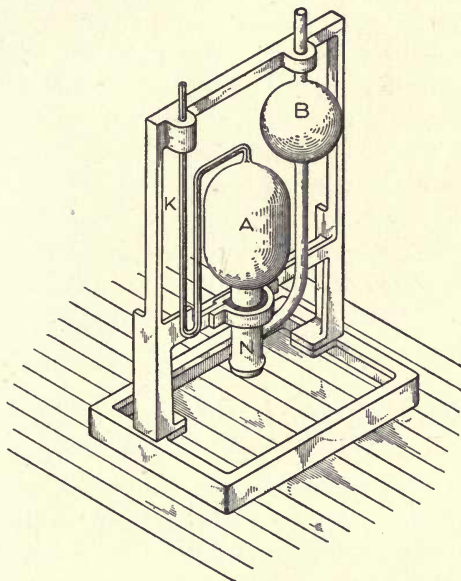


FIG. 35

A (Fig. 35), which can be filled with solid substances through the neck *N*. This neck is closed by a cork or rubber stopper which is held in place by a wire.

A glass tube closed at the top, and over which a rubber ring, cut from a rubber tube, is drawn, also makes a good stopper. By this arrangement only a narrow strip of rubber is exposed to the action of the reagent.

Pipettes of this form are used for the determination of oxygen by means of phosphorus (see p. 163). In such case it is necessary to protect the reagent from the action of the light when the pipette is not in use, which is done either by covering the pipette with a light box, or by making the cylinder *A* of brown glass.¹

THE HEMPEL DOUBLE ABSORPTION PIPETTES

Reagents that are acted upon by oxygen, *i.e.* alkaline pyrogallol, cuprous chloride, ferrous salts, etc., cannot of course be kept in the above forms of pipette, since the reagent would become inactive in a short time through contact with the air. Hempel first sought to avoid this difficulty by protecting the reagent with a layer of high-boiling petroleum, after first convincing himself that the tension of the petroleum, resulting from its solubility in the reagent, did not cause a perceptible error. It was soon found, however, that although such hydrocarbons lessen decidedly the access of air, they do not by any means form a perfect protection. Further experiment on this subject led to the construction of —

The Hempel Double Absorption Pipette for Liquid Reagents (Fig. 36)

This pipette permits the use of the reagents in question under an easily movable atmosphere that is free from oxygen, and the reagent may be kept completely saturated with those constituents of the gas that it does not strongly absorb, which is a great advantage. The pipette consists of the large glass bulb *A*, of about 150 cc. capacity, and three smaller bulbs, *B*, *C*, and *D*, each containing only 100 cc. They are connected by the bent tubes *E*, *F* and *G*, and end in the bent capillary tube *K*.

The pipette is fastened to an iron stand in the manner already described (see p. 54).

¹ Fritz Friedrichs, *J. Am. Chem. Soc.*, 34 (1912), 1513; *Z. f. angew. Chem.*, 25 (1912), 1905.

The pipette is prepared for use by slipping into the rubber tubing at *S* the tip of a burette containing the absorbing solution and allowing this to flow into the bulb *A* through the capillary *K*. The flow of the liquid through *K* may be hastened by applying gentle suction with the mouth upon a rubber tube attached to *M*. When the contents of the burette has been drawn into *A*, air is blown by the mouth through the rubber tubing attached to *M*. The

air in *A* is forced out through the capillary *K* and the burette until the liquid in *B* falls to the point *E*. The stopcock of the burette is then closed, the burette is again filled with the absorbent and the operation is repeated until the bulb *A* and the tube *E* are full. If the operation has properly been performed the absorbing liquid should fill the capillary *K*, the bulb *A*, and the con-

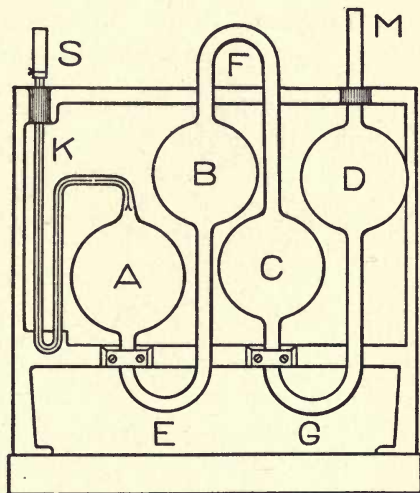


FIG. 36

necting tube *E* up to the bulb *B*, and *B* should be empty. The burette is now disconnected from *S*, and suction is applied at *M* until the absorbent is drawn up to the top of the bulb *B*, if the reagent does not absorb oxygen. *S* is then closed with a pinchcock, and water is poured into *M* until the bulb *D* is full. Upon opening *S* and gently blowing into *M* water will rise in *C* and the reagent in *A*, and if the filling has properly been performed the reagent will stand at the top of the capillary *K* when the water in the bulb *C* reaches to the top of that bulb.

If the reagent absorbs oxygen the solution should, after *A*

has been filled with it, be drawn up in *B* before the introduction of the water only to about two-thirds of the height of *B*, and the bulb *D* filled with water in the manner already described. Upon the absorption of the oxygen from the air by the reagent in the bulb *C* there will remain between the liquids in the bulbs *B* and *C* the desired volume of gas, about 100 cc.

The Hempel Double Absorption Pipette for Solid and Liquid Reagents (Fig. 37)

The construction may easily be understood from the figure. To prepare this double pipette for use, turn it upside down, introduce through the neck *N* of the bulb *A* the solid substance to be employed, close the neck with the stopper, and wire the stopper in place. Bring the pipette into an upright position and fill it with liquid in the manner described above.

While the reagent in the simple pipette may be considered to be saturated with gas only when it is kept in continual use, that in the double pipette, on the contrary, remains saturated for an exceptionally long time, since the diffusion must take place through the confining 100 cc. of water and through the narrow tube that connects the bulbs *C* and *D*. The error caused by this theoretical possibility may be wholly disregarded in using the pipette.

When the pipettes are not in use the rubber tubing on the capillary should be closed by the insertion of a short piece of

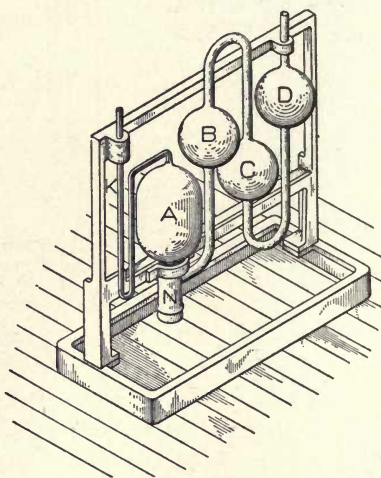


FIG. 37

glass rod. A pinchcock should not be left on this rubber tubing, since it causes rapid deterioration of the rubber. The open end of the single pipettes may be closed by the insertion of a small cork.

MANIPULATION OF THE HEMPEL APPARATUS

If the burette has been in use clean it thoroughly, and rinse it well with water. Examine the rubber tubing attached to the capillary of the burette to see that it is intact and that the wire ligature is in good condition. Make sure that the pinchcock closes the rubber tubing completely. Open the pinchcock *E*, Fig. 38, and slip it down over the capillary tube. Pour into the open end of *B* water that has been saturated with the gas mixture that is to be analyzed until *A* and *B* are rather more than half full.

Saturation of Confining Water. — A simple method of saturating the water with the gas is to place the water in a washing flask and run the gas through the flask until the air has been displaced, and to then close the exit tube and shake the contents of the flask vigorously.

Filling Burette with Confining Liquid. — Drive out all air from the large rubber tubing connecting *A* and *B* by raising and lowering the tubes alternately, keeping the rubber tubing taut during this operation. Grasp the iron base *D* in the left hand and raise it until the water begins to flow out of the top of the burette. Then close the rubber tube of the burette with the pinchcock, setting the pinchcock up close to the end of the capillary. Compress the rubber tubing at *D* between the thumb and fingers of the left hand and pour out the excess of water that is in *B*.

Measurement of 100 cc. — To measure off exactly 100 cc. of the gas sample, insert into the rubber tube at the top of the burette a capillary tube connected with the gasometer or pipe from which the sample is to be taken, after first displacing the air in this connecting capillary by the gas to be examined.

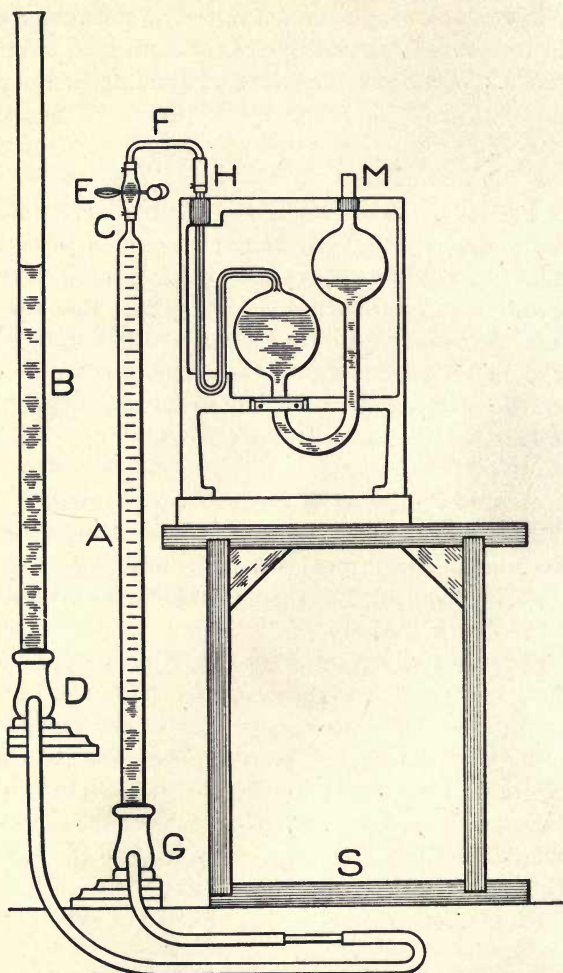


FIG. 38

Grasp the upper part of the level-tube *B* in the left hand. Lower it below *A* and open the pinchcock *E* with the right hand. Draw somewhat more than 100 cc. of gas into the burette. Close

the pinchcock *E*, place the level-tube on the table and allow the water in the burette to run down for one minute.¹ Disconnect the capillary tube from the gasometer, raise the level-tube with the right hand until the gas in the burette is compressed to a volume less than 100 cc. and then close the rubber tubing at *G* tightly by squeezing it close up to the lower end of the burette between the thumb and first finger of the left hand. Place the level-tube on the table, grasp the iron base of the burette with the right hand and keeping the rubber tubing at *G* still tightly compressed raise the burette until the meniscus of the water in it is on a level with the eye. Then gradually release the pressure on the rubber tubing until the water in the burette falls exactly to the 100 cc. mark. Keeping the tubing still compressed, place the burette on the table and open the stopcock *E* for a moment to permit the excess of gas to escape. The burette should now contain 100 cc. of the gas under atmospheric pressure. To ascertain whether this is the case, grasp the base of the burette in the right hand and of the level-tube in the left hand and holding the burette perpendicularly lay the level-tube at an angle across it, and bring the water in the two tubes to the same level. If the measurement of the sample has properly been made the water in the burette will stand exactly at the 100 cc. mark.

Absorption of a Gas. — To remove an absorbable constituent of the gas the burette and proper absorption pipette are connected in the manner shown in Fig. 38. Place the burette and level-tube on the table, the level-tube *B* at the left, bring up near the side of the burette the wooden stand *S*, and place on the stand a pipette containing the proper absorbent. Insert in *H* the bent glass capillary tube *F*. These connecting capillary tubes are of the same dimensions as the capillary tubes of the burette and pipette, namely, 6 mm. external diameter and one mm. bore. The horizontal portion is about 6 cm. long and the legs each about 2.5 cm. long. Slip a piece of rubber tubing about

¹ See p. 68.

30 cm. long over the tube *M* of the pipette. Grasp *F* between the thumb and fingers of the right hand, squeeze the rubber tube *E* on the capillary of the burette between the thumb and fingers of the left hand, blow gently through *M* until the liquid in the pipette is driven to the farther end of the connecting capillary tube *F* and then insert the end of *F* into the rubber tube on the burette. If the connection is properly made there will be practically no movement of the reagent in the connecting capillary tube.

Even if a linear centimeter of air should appear in the capillary, the error arising therefrom may be disregarded, since capillary tubing with a bore of about one mm. contains only about .01 cc. in one linear cm. If, however, after *F* has been inserted in *E*, more than a linear centimeter of air appears in *F*, it shows that the connection was carelessly made, and *F* should be slipped out of *E* and the operation repeated.

Certain reagents should never be allowed to come into contact with the rubber tube at *H*. In such case the liquid is forced upward in the capillary of the pipette until it stands just below the iron of the frame. If quite accurate results are desired, allowance should be made for the very small amount of air thus left in the connecting capillary tubes. This may easily be done by measuring the length of the capillary tube that is empty of liquid. Every ten centimeters of length corresponds to 0.1 cc. of air. This correction is not necessary in ordinary technical analysis.

When the pipette and burette have been connected in the manner above described the pinchcock on *E* is opened, the level-tube *B* is slowly raised and the gas is driven over into the pipette. Water is allowed to flow into the capillary *F* until it reaches the point in the bend of that tube to which the reagent had been driven over. The pinchcock at *E* is then closed. This manipulation leaves the capillary tube of the pipette and the greater part of the bent connecting capillary tube filled with the gas mixture under examination together with such portion

of the reagent as adheres to the walls of these capillary tubes. This adhering reagent suffices to remove the greater part of the absorbable constituent in the gas mixture because a slender column of the gas stands in contact with a comparatively large surface of the reagent, but even if the absorbable constituent should constitute 40 per cent of the gas mixture, and only half of this gas in the capillary tubes should be absorbed by the reagent on the walls, the error thus caused would be negligible in technical analysis. This is apparent when we consider that the total length of the two capillary tubes is about 40 cm. and that the volume of gas in these tubes is, consequently, about 0.4 cc. The volume of the absorbable constituent would then amount to 0.16 cc. and if only half of this were absorbed the error would be 0.08 cc. These figures illustrate an extreme case. If the absorbable constituent amounted to not more than 20 per cent of the gas mixture and if, as may usually be expected, 80 per cent of it were absorbed, the error due to incomplete removal of this constituent in the capillary tubes would be less than 0.02 cc. After the constituent that is to be removed has been entirely absorbed, the gas is drawn back into the burette. This is done by grasping the level-tube with the left hand and bringing it into such position that the confining liquid in it stands slightly lower than that in the burette. The pinchcock *E* is opened, the level-tube is slowly lowered and the gas is drawn back into the burette until the liquid from the pipette reaches the same point in *F* at which it originally stood. The pinchcock *E* is now closed, the water in the burette is allowed to run down for one minute, and the gas volume in the burette is then read in the manner above described.

It frequently happens that complete absorption of the gas can be accomplished only by shaking the pipette after the gas has been driven over into it. In such case a second pinchcock is placed on the rubber tube *H*, and after the gas has been transferred to the pipette, both *E* and *H* are closed. The frame of the pipette is now grasped in the right hand, the burette is

steadied with the left hand, and the absorbent is brought into intimate contact with the gas by gently rocking the stand backward and forward on the front edge of its base.

If the reagent has no appreciable effect upon rubber, much time may be saved in making the connection between pipette and burette by preparing the pipette in such manner that it will stand ready at all times for connection with the gas burette. This is done by placing a pinchcock upon the rubber tube of the pipette, inserting into this tube the bent connecting capillary tube, and then, holding the pinchcock open, driving the reagent over nearly to the further bend of this connecting capillary by blowing into the large rubber tube attached to *M*. The pinchcock is then closed. If the operation has been correctly performed, the reagent should now stand close to the bend in the connecting capillary tube that is nearest the burette. The capillary tube is next inserted in the rubber tube of the burette and the absorption is made in the manner above described. After the absorption of the gas, the reagent is drawn over nearly to the further bend of the connecting capillary tube, and the pinchcock on the pipette is then closed. This should drive the reagent to about the same point in the connecting capillary as that at which it first stood. The capillary tube is now withdrawn from the rubber tube that is attached to the top of the burette, and the pipette is removed. The pipette, with the bent capillary tube attached to it, now stands filled with the reagent to the further bend of the connecting capillary and is ready for immediate connection with the burette when another determination of the same constituent gas is to be made.

The manipulation of the pipettes filled with solid absorbents is still simpler, for in this case no shaking is necessary because of the large surface of contact between the solid and the gas. On this account also the apparatus need not be disconnected.

The Hempel apparatus for technical gas analysis possesses many points of superiority over other forms of apparatus. It is not fragile and if a part is broken it is easily replaced. It

contains no stopcocks. It is easily cleaned. Either water or mercury may be used as the confining liquid. When water is employed, it is easily saturated with the gas mixture under analysis. The pipettes avoid waste of reagent and protect the reagents from the air. The removal of absorbable constituents of a gas mixture may rapidly and completely be effected.

Absorbing Power of a Reagent. — If the absorbing power of the reagent is known, waste may be avoided, and with one filling of the pipette several hundred analyses (the number depending upon the nature of the gases examined) may be made, with certainty throughout as to the efficiency of the absorbent.

To determine the absorbing power of a reagent, Hempel uses a pipette of the form shown in Fig. 39. The pipette is filled with mercury, and then one cc. of the solution of the reagent is drawn in through the capillary *d*. Mercury is allowed to follow the solution so that the reagent is inclosed between the mercury in the pipette and the mercury standing in the capillary. The pipette is connected by means of rubber tubing and a bent capillary tube with a Hempel burette containing the gas under consideration. The gas is drawn into the pipette and shaken with the reagent as long as rapid absorption takes place. It is then passed back into the burette and measured. The absorbing power of the reagent thus experimentally determined is much higher than could safely be relied upon in actual gas analysis, and consequently under the assumption that only a fourth of the active reagent should be used up if there is to be no doubt as to its absorbing power, the result in each case is divided by four and the figure thus obtained is termed the *analytical absorbing power* of the reagent. This figure, of course, refers to the absorbing power of one cc. of the reagent. To illustrate, one cc. of a 33 per cent solution of potassium hydroxide was found to absorb readily 160 cc. of carbon dioxide. The analytical absorbing power of a solution of potassium hydroxide of the above strength is consequently stated to be

40, which means that one cc. of the reagent may be relied upon to absorb 40 cc. of carbon dioxide in gas analytic work.

If an accurate account is kept of the amount of gas that the

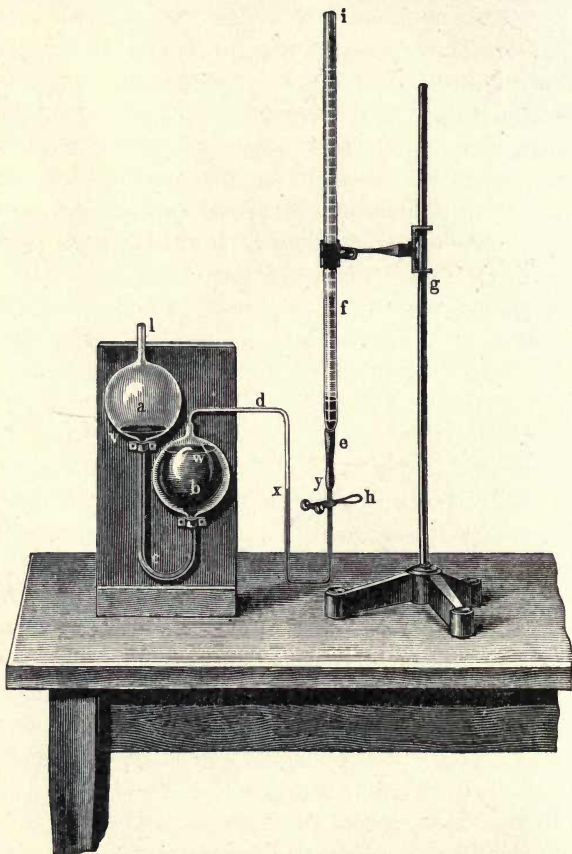


FIG. 39

reagent in a pipette has absorbed, the efficiency of the reagent still remaining in a pipette is always known, and the absorbent can be used to the full extent of its analytical absorbing power without uncertainty as to the accuracy of the analysis.

Accuracy of Analyses with the Hempel Apparatus. — The criticism has been urged against the Hempel apparatus that it is cumbersome, and that as a consequence rapid analytical work cannot be performed with it. Those who are familiar with the manipulation of the various standard forms of apparatus for technical gas analysis will, however, probably concur in the statement that an analysis of any of the usual gas mixtures can be performed with the Hempel apparatus with as great or even greater speed than that attainable with almost any other device, and with an accuracy far surpassing that of most other technical methods and approximating that obtained over mercury. This is shown by two partial analyses of illuminating gas:

I. Technical Analysis	II. Technical Analysis	Exact Analysis over Mercury
1.6 per cent	1.5 per cent	1.5 per cent carbon dioxide
3.1 “	2.9 “	3.0 “ heavy hydrocarbons
1.4 “	1.6 “	1.4 “ oxygen

It should be borne in mind, however, that with the Hempel apparatus for technical gas analysis, as with any other form of apparatus, errors so large that they may entirely destroy the value of the analysis will result when the reagents and the confining water do not have the temperature of the laboratory or when there is appreciable change in temperature during the brief time necessary for the analysis. A rise of temperature of only one degree would cause an error of 0.3 % in a total volume of 100 cc., which makes it evident that the analysis should be made in a laboratory that is of nearly constant temperature, or, if the work must be done outside of the laboratory under fluctuating temperature, the burette should be surrounded with a water jacket. The jacketing of the Hempel burette may easily be effected by slipping down over the burette an inverted single bore rubber stopper about 4 cm. in diameter, and slipping over the burette and upon the stopper a large glass tube somewhat shorter than the burette, holding the upper end in

place by means of a split cork. The larger tube is then filled with water.

Running Down of Confining Liquid. — It is also of importance, if accurate results are desired, that the confining liquid over which the gas is measured be allowed to flow down the walls of the burette in exactly the same manner and for the same length of time after each absorption. If the tube of the Hempel burette is clean, the running down of water is practically complete in three minutes. If the burette is allowed to stand two minutes longer and the water given five minutes in all to run down, the meniscus will stand from .02 to .03 cc. higher than after three minutes, a difference that is negligible in technical gas analysis with water as the confining liquid. In the description of the manipulation of the apparatus on page 61 it was stated that the water should be allowed to run down for one minute. The results will naturally be more accurate if the three minute interval is employed, but for technical analyses where speed is a desideratum and great accuracy is not necessary, much time may be saved by making the readings only one minute after the gas has been passed back into the burette. The following analyses made by Dr. R. P. Anderson in the Cornell Laboratory show the variation in the results when the water in the burette is allowed to run down one, two, three and five minutes.

Determination of Oxygen with the Phosphorus Pipette
August 8, 1911

	1 Minute	2 Minutes	3 Minutes	5 Minutes
I	20.6	20.7	20.8	20.8
II	20.6	20.7	20.8	20.8
III	20.6	20.7	20.8	20.8

In apparatus in which gas volumes are read over liquids other than water or mercury, such as solutions of fixed alkalis, cuprous chloride, alkaline pyrogallol, and the like, the running down of the liquid takes place slowly, and an error in measure-

ment of one cubic centimeter or more may result if the reading is not made under exactly the same conditions in all cases. While distilled water will run down completely in a Hempel burette in five minutes, a five per cent solution of sodium hydroxide requires ten minutes and concentrated sulphuric acid

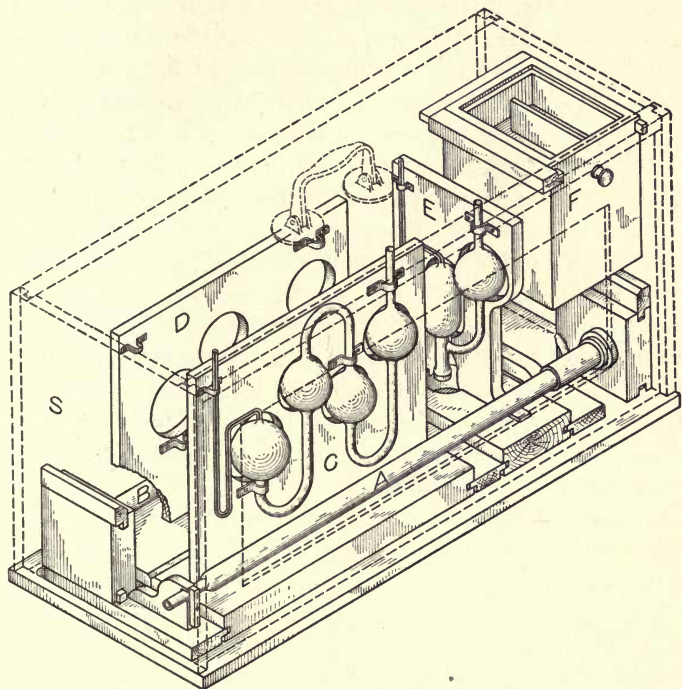


FIG. 40

from fifteen to twenty minutes. If in an analysis of a gas mixture the residual gas volumes are read first over one liquid and then over another, it is apparent that rapid and at the same time accurate work is almost if not quite impossible.

Portable Hempel Apparatus. — It must be conceded that the Hempel apparatus is not easy to carry about, but for the analysis

of rather simple gas mixtures this objection is obviated by the portable Hempel apparatus devised by the present writer and shown in Fig. 40. The burette *A* has a capacity of 50 cc. and is calibrated in one-fifth cc. It is set in a square iron base that is grooved on two sides and slips over the wooden guides shown in the drawing. The level-tube *B* is similarly mounted and lies on the bottom of the case opposite the burette. The case contains three Hempel gas pipettes, one, *E*, a simple pipette for solid reagents, and two, *C* and *D*, double pipettes for liquid reagents. These pipettes are mounted on wooden frames to lessen the weight of the apparatus. The apparatus may be obtained with pipettes of different forms than those here given if the analyst should so desire. The drawer *F* contains small accessories such as rubber tubing for connections, and the bent capillary tubes for joining the burette with the pipettes. The front and the back of the case are fitted with sliding covers, and the top is provided with a metal handle. The apparatus is quite compact, the dimensions of the outer case being 20.5 cm. long, 11 cm. high, and 8 cm. wide. The total weight of the apparatus when the pipettes are not filled is 6.8 kilograms.

It was formerly necessary to analyze gas mixtures containing carbon dioxide at the place where the sample is taken, because of the difficulty of obtaining a proper average sample of a gas mixture containing this ingredient and of transporting it to the laboratory without change in its composition. The Huntly sample tube described on p. 5 appears to remove this difficulty.

THE MODIFIED WINKLER GAS BURETTE (Fig. 41)

This gas burette is of use in the determination, directly in the burette, of gases that are readily soluble in water, such as ammonia or hydrogen chloride. Yet when a gas mixture contains gases that are easily soluble in water, it is generally preferable to pass a large volume of the gas mixture through a

suitable absorbent, and to then determine the absorbed gas by titration.

The Winkler burette consists of the level-tube *a* and the measuring tube *b* connected by a rubber tube about 120 cm. long and fastened into iron feet. *b* is a glass tube of about 100 cc. capacity, provided with the three-way cock *c* and the simple glass stopcock *d*. The space between the two stopcocks is divided into exactly 100 equal parts, and each part into fifths. The capillary *e* has the same dimensions as that on the Hempel burette. Instead of the glass stopcock *d* a rubber tube and pinchcock may be used as with the simple burette.

Manipulation of the Winkler Burette.—Before filling the burette with the easily soluble gases, the tube *b* is first dried by rinsing it out with a few cubic centimeters of absolute alcohol and then with ether, the latter being driven out by aspirating through the tube the gas to be analyzed. To do this, join the end *e* of the burette by means of a rubber tube, or better a glass tube, to the vessel containing the gas and bring the three-

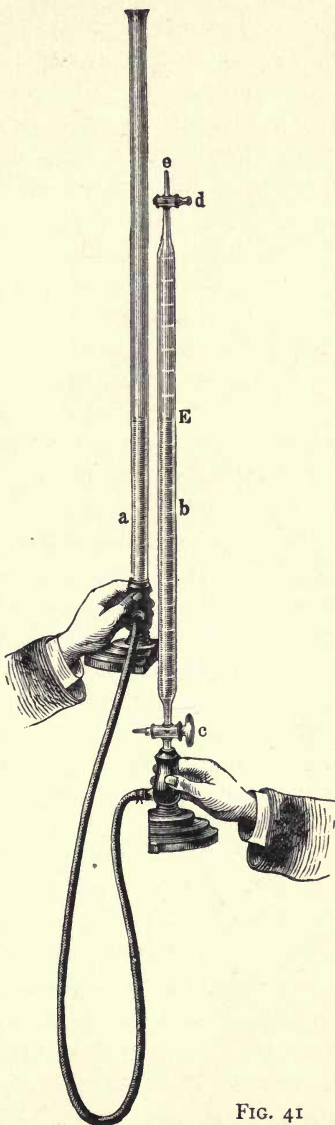


FIG. 41

way cock into such a position that its longitudinal opening communicates with the inside of the burette. Connect the cock with the aspirator. After the gas has been drawn through for a time, close the upper stopcock and turn the lower stopcock through an angle of 180° . Place upon the tail of the lower (three-way) stopcock a short piece of rubber tubing and close this with a pinchcock. The gas, if under pressure, is brought to atmospheric pressure by momentarily opening the upper stopcock. The remainder of the apparatus is now filled with water run in through the three-way cock, which is so turned that it communicates with the rubber tube. The water must previously be saturated with those constituents of the gas mixture which are slightly soluble in water. The easily soluble gas in the mixture is then absorbed by turning *c* into such position that *a* and *b* are connecting, allowing some water from *a* to rise in *b*, closing *c* and, with *b* held in a horizontal position, running water backward and forward to promote the absorption of the gas. *b* is then placed in an upright position, *c* is opened and the residual gas volume is read. *c* is then closed and the gas in *b* is shaken again with the water, and after opening *c* the volume is again read. This is continued until no further diminution of the gas volume in *b* takes place. The constituents that are only slightly soluble in water are determined by absorption in the Hempel pipette in the usual manner.

THE HONIGMANN GAS BURETTE

The Honigmann gas burette is suited only to the rapid and approximate determination of carbon dioxide in gas mixtures that contain fairly high percentages of this constituent.

The burette *A* (Fig. 42) contains 100 cc. divided into $\frac{1}{5}$ cc., the zero point being at the lower end of the burette. At the top it is closed by a glass stopcock and the lower end below the graduation is drawn out to smaller diameter to permit of a piece of rubber tubing being easily slipped over it. The

absorbing liquid, potassium hydroxide, is placed in a glass cylinder *c*, which should be tall enough to allow the burette to be lowered to any desired point into the liquid.

Manipulation of the Honigmann Burette. — In making a determination, the burette is first thoroughly cleaned with water, and the gas to be analyzed is then passed through it until all air in the burette has been displaced. Stopcock *a* is now closed and the rubber tube is immersed in a solution of potassium hydroxide in the manner shown in the figure. The solution of potassium hydroxide contains one part of commercial potassium hydroxide dissolved in two parts of water. The burette is lowered into this solution until the liquid stands exactly at the zero point. The stopcock *a* is then carefully opened until the liquid inside the burette rises to the same mark, and it is then closed. The tube now contains 100 cc. of the gas at atmospheric pressure. The absorption of the carbon dioxide is effected by grasping the burette between the thumb and fingers in the manner shown in the figure, and turning it downward so that the caustic potash will flow along the walls of the burette. During this operation the open end of the rubber tube must, of course, remain below the surface of the solution in the cylinder.

After all the carbon dioxide has been absorbed, the burette is again brought to a perpendicular position and is lowered into the liquid in the cylinder until the liquid surfaces on the inside and outside of the burette stand at the same height. The reading

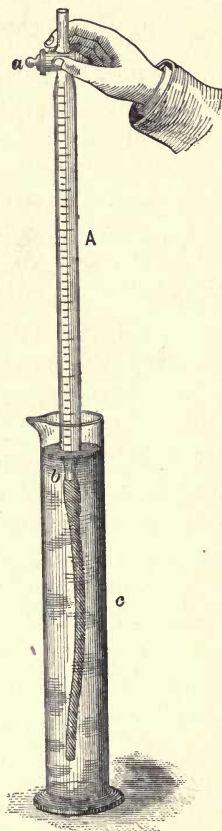


FIG. 42

is now taken, and the result gives directly the percentage amount of carbon dioxide present in the original gas mixture.

THE BUNTE GAS BURETTE

The Bunte burette may be used for the approximate determination of carbon dioxide and oxygen.

The burette *A* (Fig. 43) is closed at the top by the three-way stopcock *C*, and above this there is the tube *D*, which is provided with a mark about 5 cm. above the stopcock. The lower end of the burette is closed by a simple glass stopcock, and is connected with the level-bottle *B* by a long piece of rubber tubing. A pinchcock is placed upon this rubber tube a short distance below the end of the burette. Inasmuch as all of the readings with this burette will probably lie between the zero point and the 50 cc. mark, the instrument is made shorter, and consequently easier to handle, by widening the upper portion. The horizontal opening of the stopcock *C* is closed by a piece of rubber tubing and a pinchcock. The burette and level-bottle are supported on an iron stand of the form shown in the figure, the burette being held in a spring clamp which permits of its easy removal. The calibration of the burette runs from the zero point, which is near the lower end, up to 100 cc. at the upper stopcock. The calibration is carried on below the zero point for 10 cc. There must also be provided a thick walled glass bottle *S* supplied with a one-hole rubber stopper carrying a short piece of glass tubing which is closed by a piece of rubber tubing and a screw pinchcock. A piece of glass tubing bent in the shape Ω is also necessary for running water into *D*.

Manipulation of the Bunte Burette. — Fill the level-bottle *B* with water, connect the rubber tube with the burette in the manner shown in the figure, open the pinchcock *H* and the two stopcocks of the burette, and allow water to rise in the burette until *D* is partially filled. Close *G* and *H*. Now turn the stopcock *C* until *D* communicates with *F*, and open

the pinchcock on *F* until the bore of the stopcock and the rubber tube are filled with water. Then close the pinchcock. Slip the pinchcock *H* up to the lower end of the burette. Close it, and remove the long rubber tube from the burette. Place under the burette a beaker to catch the water which runs out. Connect *F* with the reservoir containing the gas to be analyzed, and open the pinchcock on *F* and the lower glass stopcock of the burette. The water in the burette will now flow out, and the gas will be drawn over into the tube. Draw into the burette rather more than 100 cc. of gas.

The gas in the burette is always read at the pressure of the atmosphere plus the pressure of the column of water standing in *D* up to the mark. For convenience in calculating results it is desirable that the original volume be exactly 100 cc. at this pressure. To measure off this exact volume close the stopcock *C*, open the pinchcock *H* until the long

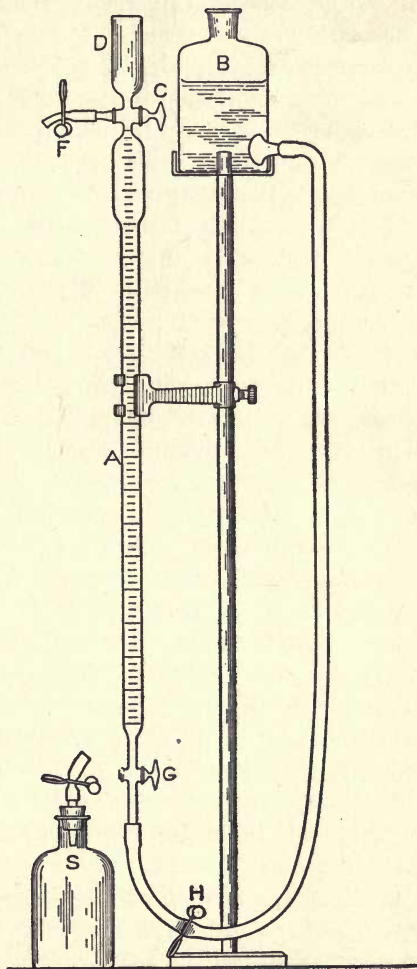


FIG. 43

rubber tube is filled with water, and then slip this carefully over the lower end of the burette, after first making sure that there are no bubbles of gas in the tip of the burette below the stopcock. Now open *H* and *G*, and allow water to rise nearly to the zero point. Close *G*, and then turn *C*, so that *A* communicates with *D*. Since the gas in the burette is under slight pressure, bubbles will escape upward through the water in *D*. Bring the water in *D* exactly to the mark, and then by carefully opening *G* allow the water in the burette to rise until it stands exactly at zero. There is now in the burette 100 cc. of gas under the pressure of the atmosphere plus the column of water in *D*. Close *C*, and proceed to the absorption of the constituent of the gas mixture that is to be determined.

This absorption is brought about by introducing a liquid absorbent into the burette through the lower end. Since these absorbents for the various gases are usually concentrated solutions, it is undesirable to allow the absorbent to be diluted by the water still remaining in the burette between *G* and the zero point. This water is therefore first removed with aid of the suction bottle *S*. This bottle is connected by means of the rubber tube at its top with a water suction pump, and is exhausted of air. The screw pinchcock is then closed, the long rubber tube is slipped off from the lower end of the burette, and the rubber tube of *S* is slipped over the burette tip. The screw pinchcock on *S* is now opened, *G* is then carefully turned, and the water in the burette is slowly drawn off until it has fallen to a point just above *G*. *G* is then closed, the pinchcock of *S* is closed, and the suction bottle is detached. This operation serves also to bring the pressure of the gas in the burette below that of the atmosphere, and thus renders it possible to introduce the reagent through the lower end of the burette. The reagent to be introduced into the burette is now poured into a small evaporating dish, and this dish is brought up under the tip of the burette; *G* is carefully opened, and the liquid at once rises

in the burette. When no more will enter, close *G*, remove the dish, grasp the burette with the thumb and the first two fingers of the left hand at the stopcock *C*, and open the spring clamp with the right hand. Place the first and second fingers of the right hand below the stopcock *G*, pour out the water in *D*, and tip the burette backwards and forwards so that the absorbing liquid will flow along its entire length. Place it again in the clamp, bring the dish of the absorbent under the tip, and allow more liquid to enter if it will, repeating the tilting of the burette in the manner just described. When the absorbent will rise no farther in the burette, that is, when the absorption of the gas is completed, place the burette in the clamp in such a position that its upper end is below the level-bottle *B*, put a beaker under *G*, and insert in the end of the rubber tube of *B* the Ω -shaped glass tube already mentioned. Hook this tube over the edge of *D*. Open the pinchcock *H* so that water will flow into *D*, then open *C*, and lastly open *G*. Water will now flow through the burette and wash out the absorbent, and yet no gas will escape during the operation. When the absorbent has been removed in this manner, close *G*, shut off the supply of water from *B*, and then carefully open *G* until the water in *D* falls just to the mark. Read the volume of gas now remaining in the burette. The difference between this volume and the original volume of 100 cc. will give the per cent of gas which has been absorbed. The same procedure is followed in the determination of a second constituent in the same sample.

Throughout the entire operation be sure not to touch with the hand any part of the burette except the two stopcocks, since otherwise the heat of the hand would expand the gas in the burette and cause some of it to escape through the open stopcock *C*.

Determinations with the Bunte burette cannot be accurate, since the gas in the burette is brought into contact with large volumes of water that is unsaturated with the gas mixture, and which will therefore absorb some of the gas of the sam-

ple.¹ The method is also wasteful of reagent, since the reagent which has once been employed cannot be used over again because of its dilution by the wash water.

THE ORSAT APPARATUS

In the analysis of commercial grades of sodium carbonate there early arose a demand for a rapid and convenient method for the determination of carbon dioxide, which was met in 1868 by the apparatus designed by Schlösing and Rolland.² In 1874 Orsat patented a device³ that was based directly upon the principle of the apparatus of Schlösing and Rolland, and that attracted considerable attention at the time and rapidly came into general use. Because of its compactness and ease of manipulation the Orsat apparatus has been and still is very generally employed by gas analysts. In its original form, however, and even in some of the later modifications it possesses certain inherent faults, and the unsatisfactory character of the analytical results that are obtainable with the various forms is evidenced by the large number of changes in its construction that are constantly being brought forward in chemical journals. The chief objection to the apparatus is the incompleteness of the absorption of such gases as oxygen and carbon monoxide. The researches of Gautier and Clausmann, Bendemann, Hankus, Hempel, Nowicki, Hahn, Dennis and Edgar and others have demonstrated that the complete removal of oxygen by alkaline pyrogallol and of carbon monoxide by cuprous chloride can be effected only when the absorbent and the gas are shaken together, or when the gas is, in some manner, brought into prolonged and intimate contact with the absorbent. With most

¹ The manner of manipulation of the Bunte burette described by Haber in the *Journal für Gasbeleuchtung*, 39 (1896), 802, lessens the errors due to the absorption of the gases by the wash water, but is probably too inconvenient to be generally followed. If the burette is used in the customary manner, it does not give accurate results.

² *Annales de chimie et de physique*, 4 serie, 14 (1868), 55.

³ *Chem. News*, 29 (1874), 177.

of the suggested forms of the Orsat absorption pipette, the removal of oxygen and carbon monoxide is quite incomplete unless the gas is allowed to stand in contact with the absorbent for a very considerable length of time, or is passed back and forth many times between the burette and pipette. Failure to recognize this inadequacy of the apparatus frequently results in the incomplete removal of oxygen, and, as a consequence, a decrease in volume is observed when the gas mixture is next passed into the cuprous chloride pipette. In very many cases the analyst has in this manner been led into reporting carbon monoxide in a gas mixture, such as flue gas, when in fact no carbon monoxide is present, the decrease in volume being due solely to the absorption, by cuprous chloride, of oxygen that still remains in the gas mixture.

In recent years several interesting and some valuable suggestions for increasing the completeness and rapidity of absorption in the Orsat apparatus have appeared in chemical journals. Bendemann proposes ¹ that two pipettes be used for the absorption of oxygen by alkaline pyrogallol and two for the removal of carbon monoxide by cuprous chloride. This would undoubtedly lessen the errors of the determinations but would hardly remove them entirely. More worthy of consideration are the proposed modifications of the form of the absorption pipette to bring gas and liquid into intimate contact. Most of these are based upon the construction described in 1899 by E. Hankus ² and shown in Fig. 44. The gas enters the pipette through *A*, passes downward through the capillary and, by impinging on the plate *B*, is broken up into minute bubbles which then pass upward through the absorbing liquid. The gas is brought back into the burette by turning the stopcock through an angle of 180° and lowering the level-bottle of the burette.

In 1911 the Chemists' Committee of the United States Steel

¹ *Jour. f. Gasbeleuchtung*, 49 (1906), 853.

² *Österr. Chem. Ztg.*, 47 (1899), 81; *J. Gasbeleuchtung*, 49 (1906), 367.

Corporation described ¹ an absorption pipette (Fig. 45) that is quite similar to the form proposed twelve years earlier by Hankus, but is slightly less efficient than the Hankus pipette (see results below) since it permits the gas to escape freely in large bubbles from the lower end of the capillary tube.

The pipette devised by Nowicki ² and improved by Heinz ³ (Fig. 46) yields more complete absorption than that of Hankus.

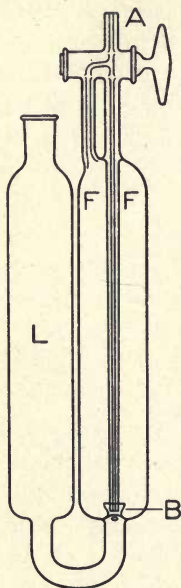


FIG. 44

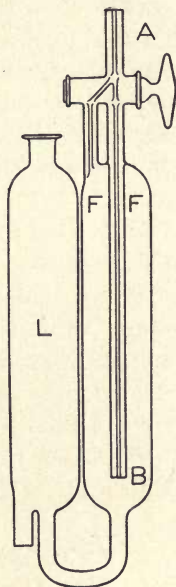


FIG. 45

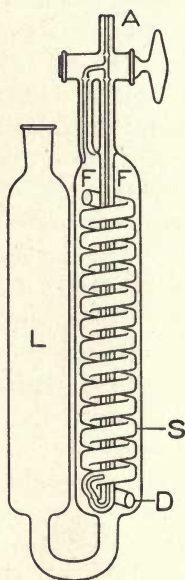


FIG. 46

The gas passes downward through the straight capillary tube *A* and then rises in small bubbles through the spiral tube *S* which insures long and thorough contact between the gas and absorbent. A short tube *D* is attached to the lower end of the spiral, and fresh absorbing liquid is drawn upward through this open-

¹ *Met. and Chem. Eng.*, **9** (1911), 303.

² *Österr. Zeit. f. Berg.-Hütt.*, **53** (1905), 337.

³ *J. Gasbeleuchtung*, **49** (1906), 367.

ing when the gas bubbles rise through the spiral. Experience has shown, however, that when this form of absorption pipette is used for the determination of oxygen with alkaline pyrogallol the gas is frequently trapped in the spiral. Moreover, the pipette is so fragile that it is often broken in transportation, which renders it unsuitable for use in a portable apparatus.

The very rapid and complete absorption of gases that upon experiment was found to be obtainable with the Friedrichs gas washing bottle¹ led the author to employ the same principle in the construction of an absorption pipette for the Orsat apparatus, the form of pipette that was finally adopted being that shown in Fig. 47. The gas mixture enters the pipette through the capillary *A* (the stopcock being in position I), and, passing downward through the capillary, escapes at *B*. It then rises and in so doing follows the spiral *S*. The rising gas carries some of the absorbing liquid with it, and this liquid then flows down on the inside of the cylinder *C* and mixes with the main body of the absorbent again at *D*. After the gas has risen through the spiral and has collected in the space *F*, the stopcock is turned through 180° to position II and the gas is then drawn back into the burette.

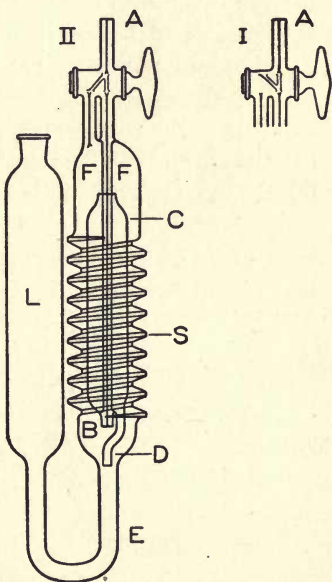


FIG. 47

An experimental comparison of the different forms of Orsat pipette here illustrated has been made by Mr. F. H. Rhodes. In the first series of comparative determinations oxygen in

¹ *Z. anal. Chem.*, 50 (1911), 175.

atmospheric air was absorbed by means of an alkaline solution of pyrogallol. (See p. 160). One hundred cc. of air was measured off in a Hempel burette, and this was then connected with the pipette under examination, and the gas sample was passed back and forth between the absorption pipette and the burette until all of the oxygen in the sample had been absorbed. The air was passed into the several pipettes at a uniform speed. The absorption pipettes that were tested were

- (a) the usual form of Orsat pipette, which is filled with glass tubes to increase the absorbing surface;
- (b) the Hankus pipette (Fig. 44);
- (c) the absorption pipette recommended by the Chemists' Committee of the United States Steel Corporation (Fig. 45);
- (d) the Nowicki-Heinz spiral absorption pipette (Fig. 46); and
- (e) the new form of pipette here described (Fig. 47).

TABLE I

The sample of air was passed over into each absorption pipette in one minute. It was then immediately drawn back into the burette and again passed into the absorption pipette at the same speed as before. This was continued until all of the oxygen was absorbed. The results given in the tables are the averages of numerous determinations.

Time (Minutes)	(a) Orsat Usual Form	(b) Hankus Pipette	(c) U. S. Steel Committee	(d) Nowicki- Heinz Pipette	(e) Pipette New Form
1	8.0	11.2	9.0	20.6	18.6
2	13.3	16.5	14.2	20.8	20.4
3	16.7	19.1	17.2	20.9	20.9
4	18.7	20.1	18.8		
5	19.5	20.5	19.8		
6	20.2	20.7	20.2		
7	20.4	20.8	20.6		
8	20.8	20.9	20.9		
9	20.9				

TABLE II

In the analyses here tabulated, the sample of air was first passed into each pipette in two minutes, that is, at half the earlier speed. It was then immediately drawn back into the burette and passed a second time into the pipette in one minute.

Time (Minutes)	(a) Orsat Usual Form	(b) Hankus Pipette	(c) U. S. Steel Committee	(d) Nowicki- Heinz Pipette	(e) Pipette New Form
2	10.3	15.6	12.3	20.7	20.6
1 minute more	17.2	18.3	17.2	20.9	20.9

The above results render it evident that the complete absorption of oxygen from air can be effected with the first three forms of pipette only by repeated passage of the gas sample into the pipette and back into the burette. The Nowicki-Heinz pipette and the spiral pipette here proposed seem to be of nearly equal efficiency, but the former is open to the objections already noted.

To ascertain the efficiency of the new spiral pipette in the absorption of carbon monoxide, mixtures of this gas with known amounts of air were prepared; oxygen was determined in one spiral pipette by absorption with an alkaline solution of pyrogallol and carbon monoxide in a second spiral pipette by absorption with an ammoniacal solution of cuprous chloride. In the absorption of oxygen the gas mixture was passed into the pipette in two minutes, was drawn back and then passed in a second time in one minute. In the absorption of carbon monoxide the same time intervals were found to give complete absorption of the gas unless the amount of carbon monoxide exceeded 25 per cent. In such case it was found necessary to pass the gas mixture three times into the pipette, the first time in two minutes, and the second and third times in one minute each. The results were as follows:

		I	II	III
Oxygen	{ Taken	17.7	16.2	13.2
	{ Found	17.8	16.3	13.2
Carbon monoxide	{ Taken	15.8	22.9	37.3
	{ Found	15.8	22.8	37.4

It thus appears that with this form of absorption pipette both oxygen and carbon monoxide can be removed as completely and as rapidly as is possible with the Hempel absorption pipette in which the gas and absorbent are shaken together.

A further error in analyses made with the usual forms of the Orsat apparatus results from the incorrect positions of the measuring burette.¹ After the removal of the absorbable constituents of the gas mixture the capillary tube that connects the burette with the pipettes remains filled with the combustible residue; consequently, when a portion of this residue is measured off in the burette and is passed to the combustion apparatus through the capillary tube above the pipettes, it will carry with it the combustible gas remaining in that capillary. This difficulty may be avoided by filling the connecting capillary with the confining liquid (water) in the manner suggested by Pfeifer,² or more simply by placing the burette between the absorption pipettes and the combustion apparatus in the manner recommended by Hahn.³ Since the Orsat apparatus is chiefly employed for the determination by absorption in liquid reagents of carbon dioxide, oxygen, and carbon monoxide, it is, in the opinion of the writer, preferable to limit the apparatus to the determination of these three gases and to construct it in such manner as to render it easily possible to connect the burette, when so desired, with suitable special apparatus for the determination of hydrogen and hydrocarbons. The apparatus

¹ See Hahn, *Zeit. d. Vereins deutscher Ingenieure*, 1906; *J. Gasbeleuchtung*, 49 (1906), 367.

² *J. f. Gasbeleuchtung*, 51 (1908), 523.

³ Loc. cit.

is thus rendered smaller, more easily portable, and less fragile, and the combustion results, with proper apparatus, will usually be much more accurate than with the imperfect devices contained in the many forms of the Orsat apparatus now upon the market.

A further drawback in the usual forms of Orsat apparatus is to be found in the rubber bulbs that are attached to the level-cylinders of the pipettes to protect the various reagents from the air. These bulbs rapidly deteriorate, and after short use fail to accomplish the purpose for which they are intended.

In the hope of remedying some if not all of the defects of the Orsat apparatus that have been enumerated above, the author has designed the modification shown in Fig. 48.¹

The burette *B* has a capacity of somewhat more than 100 cc. and is graduated from a point near the bottom upward to the stopcock *J*. This stopcock is a three-way stopcock, the position of which is shown by means of a black glass $\neg$ fused to its outer surface. The capillary tube connecting *J* with the pipettes and with the stopcock *K* has an external diameter of 7 mm. and an internal diameter of one mm. In fusing on the branch capillaries that extend downward to the three pipettes, the internal diameter of the capillary should at no point be much greater than one mm. if the apparatus is properly made. The three absorption pipettes *E*, *F*, and *G* are of the form already described, and are filled respectively with solutions of potassium hydroxide, alkaline pyrogallol, and ammoniacal cuprous chloride. They are connected with the capillary tube from the burette by means of pieces of soft, black rubber tubing of 1.5 mm. thickness of wall, and these rubber tubes are held in place by wire hooks that pass through the blocks behind the joints, and have threaded ends upon which small set screws are placed. This method of attachment renders it easily possible to remove all the glass parts from the frame. Into the open ends

¹ The apparatus is manufactured by Greiner and Friedrichs, Stützerbach in Thüringen, Germany.

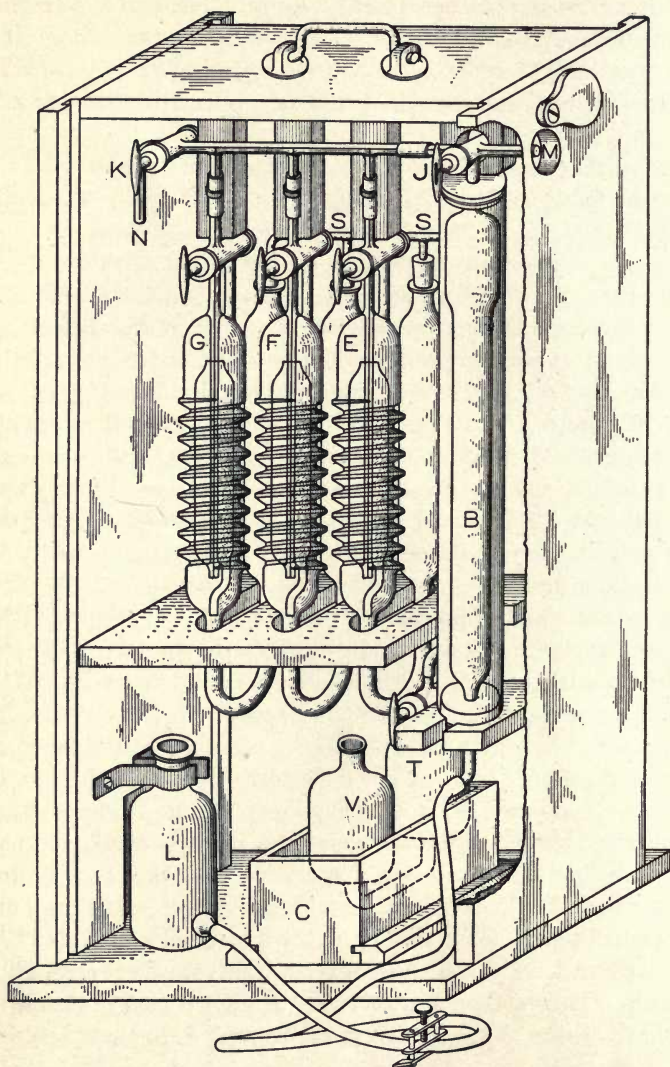


FIG. 48

of the three level-tubes of the pipettes are inserted one-hole rubber stoppers, and through the openings of these stoppers pass the branch tubes from the tube *SS* that is 7 mm. external diameter, and one mm. thickness of wall. This tube passes downward and is joined by a piece of rubber tubing to the upper side of the stopcock attached to the cylindrical vessel *T* which in turn is connected with *V* by the glass tube shown by the dotted line. After the pipettes have been filled with the several reagents, the stoppers connecting the level-tubes with the tube *SS* are inserted in place and the protecting reservoir *VT* is half filled with water. As the gas is driven over from the burette into the pipette and is drawn back into the burette, the water in *VT* rises and falls, but protects the reagents at all times from contact with the air. The level-bottle *L* is held in place by a clamp when the apparatus is in transport.

Manipulation of the Orsat Apparatus. — The level-bottle *L* is filled with water which is then driven up to the top of the burette *B* by turning the stopcock *J* to the position shown in the figure and raising *L*. The stoppers of the level-tubes of the pipettes *E*, *F*, and *G* are then removed and the solutions of the reagents that are to be used in the three pipettes are introduced into the level-tubes. The stopcock *J* is then turned so that the burette *B* is in communication with the capillary tube above the pipettes and the liquid in each pipette is drawn up almost to the lower side of the stopcock by turning the stopcock to position II, Fig. 47, and lowering the level-bottle *L*. The stopcock of each pipette is closed when the absorbing liquid in it has been raised to this point. Water is now poured into the reservoir *V* until *V* and *T* are half filled. The stoppers attached to the branch tubes of the tube *SS* are then inserted into the necks of the level-tubes of the pipettes.

The stopcock *J* is now turned to the position shown in Fig. 48 and the water in the burette *B* is allowed to run back into the level-bottle *L* and is then poured out of *L*. The level-bottle is then filled with water that has been saturated with the gas

mixture that is to be analyzed (see p. 59), and the burette *B* is filled with this confining liquid up to the mark on the capillary just below the stopcock *J*. The tube *N* is now connected with the pipe or gasometer from which the sample of gas is to be drawn, the stopcock *K* is opened and somewhat more than 100 cubic centimeters of the sample is drawn into the burette *B*. The stopcock *K* is then closed and exactly 100 cubic centimeters of gas is measured off in *B* in the manner described on p. 59, the excess pressure being released by turning *J* to the position shown in the figure. The stopcock *J* is then turned to such position that the burette *B* communicates with the absorption pipette *E*, the level-bottle *L* is raised and the stopcock of the pipette is carefully turned to position II, Fig. 47, and a small amount of gas just sufficient to drive the absorbent downward out of the left hand capillary tube below the stopcock is allowed to enter the pipette. The stopcock is then turned to position I, Fig. 47, and the gas sample is driven over from the burette into the pipette at such speed that the total sample will pass into the pipette in about two minutes. The stopcock of the pipette is then turned to position II, Fig. 47, and the gas, which now occupies the space *FF*, Fig. 47, is drawn back into the burette by lowering the level-bottle, the liquid in the pipette being carefully drawn up into the two capillary tubes below the stopcock until it stands just below the stopcock in each tube. The stopcock is then closed. In the determination of carbon dioxide a single passage of the gas into the pipette suffices for the complete removal of the constituent, and the diminution in volume is read in the burette *B* after the water has been allowed to run down for two minutes. In the absorption of oxygen by alkaline pyrogallol and of carbon monoxide by ammoniacal cuprous chloride, it is necessary to pass the gas twice through the pipette. In such case, by suitable manipulation of the stopcocks, the gas sample after being drawn back from the pipette the first time is immediately passed through it a second time. In the determination of the two gases in question the

second passage of the sample may be more rapid than the first (about one minute). The sample is then drawn back into the burette *B* and is measured in the usual manner, the water being allowed to run down one minute before each final reading.

After the absorption of the first constituent in the pipette *E*, the second is absorbed in *F* and the third in *G*. The three gases that are most usually determined with the Orsat apparatus are carbon dioxide, oxygen and carbon monoxide in the order named. The pipette *E* contains potassium hydroxide (see p. 225), *F* contains alkaline pyrogallol (see p. 160), and *G* is filled with ammoniacal cuprous chloride (see p. 232). If the gas residue contains combustible constituents that are to be determined, the combustion apparatus is connected with the capillary tube *M* and the gas in the burette *B* is driven into the combustion pipette by turning the stopcock *J* to the position shown in Fig. 48 and raising the level-bottle *L*. If only a portion of the residue is to be used for analysis by explosion, the larger part of the gas residue may be passed into the pipette *E*. The smaller portion of the gas that is to be exploded is then measured in *B*, the stopcock *J* is turned to the position shown in Fig. 48 and air is drawn in through *M* until the total gas volume amounts to nearly 100 cc. *J* is then closed, the explosion pipette is connected to *M* and the mixture of combustible gas and air is driven over into the pipette.

The case containing the apparatus is 57 cm. high, 27 cm. wide and 16 cm. deep. The panels forming the front and back of the case are removed when the apparatus is in use. As illustrative of the accuracy and uniformity of the results yielded by this apparatus the following analyses of a mixture of carbon dioxide, oxygen, and carbon monoxide may be cited.

	I	II	III	IV
Carbon dioxide, per cent	3.1	3.1	3.2	3.1
Oxygen “	6.0	6.0	5.9	5.9
Carbon monoxide, “	22.5	22.6	22.6	22.7

CHAPTER VII

THE HEMPEL APPARATUS FOR EXACT GAS ANALYSIS WITH MERCURY AS THE CONFINING LIQUID

On account of the solubility of gases in water no great accuracy is attainable when this is used as the confining liquid even when it is saturated with the gas mixture being analyzed. If very accurate results are desired, the apparatus must unquestionably be filled with mercury. Some years ago it was difficult to obtain glass stopcocks that were perfectly tight, but the manufacture of glass apparatus has been so greatly improved of late that satisfactory instruments can now easily be procured. Complete certainty that the apparatus is absolutely tight is, however, assured only by the use of apparatus that contains no stopcocks or rubber connections whatever, and in which all joints are made by fusing the glass tubes together.

A. APPARATUS WITH RUBBER CONNECTIONS AND GLASS STOPCOCKS

I. Gas Burettes with Correction for Variations in Temperature and Barometric Pressure

Pettersson¹ was the first to show that by means of a tube inclosing a volume of gas it is easy to compensate the error which would result from variations in the pressure and temperature of the atmosphere. Extreme accuracy in gas analysis can be attained by the use of apparatus that is filled with mercury and is provided with such a compensating tube, the results with such an instrument being quite as exact as those obtained with the more elaborate apparatus for exact gas analysis described on

¹ *Zeitschrift für analytische Chemie*, 25 (1886), 467.

p. 99, provided always that the stopcocks and rubber connections are perfectly tight. Three different forms of gas apparatus with temperature and pressure correction are shown in Fig. 49, the measuring tubes being varied to accommodate gas volumes of different sizes. Fig. 49, I, shows the apparatus intended for the measurement of gas volumes up to 100 cc. Fig. 49,

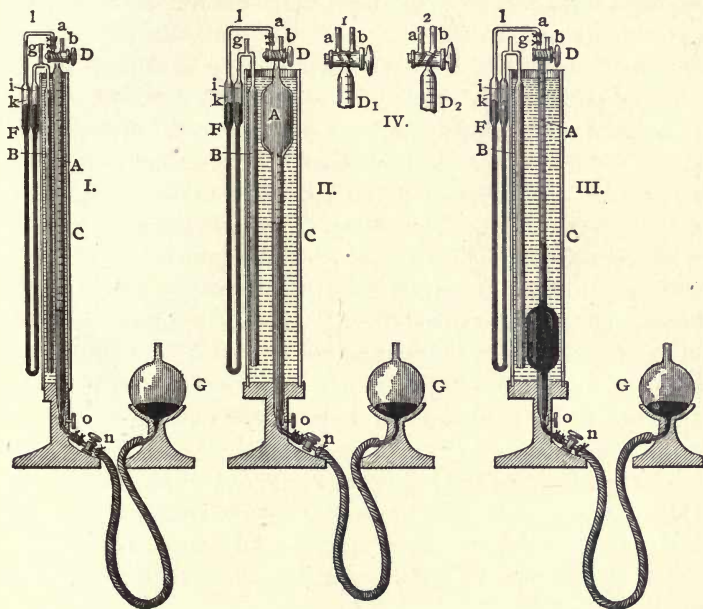


FIG. 49

II, may conveniently be used when the gas volume amounts to about 150 cc. In Fig. 49, III, is shown an instrument which was specially constructed for the examination of gases evolved from bacteria, the gas volumes here usually not exceeding 10 cc.

The instruments consist of the graduated measuring tubes *A*, the correction tubes *B*, the manometer tubes *F*, and the level-bulbs *G*. The measuring tubes and level-bulbs are mounted in suitable iron feet. The measuring tubes and the correction

tubes stand in the wide glass cylinders *C*, which are filled with water to insure that these two tubes are at all times at the same temperature. The measuring tubes are closed at the top by a double Greiner-Friedrichs glass stopcock, the construction of which is shown in Fig. 49, IV.

The correction tube *B* and the manometer tube *F* are made from plain glass tubes fused together in the form shown in the cut. *g* is a small capillary tube. The manometer tubes are U-shaped, and are somewhat widened at *k* and *i*, these two widened portions having marks scratched on the glass at exactly the same height. The manometer tube is joined to the measuring tube by means of a piece of rubber tubing connecting the end of the capillary *l* with the tube *a* of the stopcock. The reason for making the manometer tube so long lies in the fact that otherwise, if the apparatus is carelessly handled, the mercury might easily be driven from the manometer tube into the burette or the correction tube. With the arrangement shown in the figure this is almost impossible, since the difference in pressure must be more than half an atmosphere before the mercury can pass over into either tube. The manometer tube is made completely of glass to prevent the mercury being contaminated with the dirt from the interior of a rubber connection. If the burette has become dirty, the manometer tube is removed, and the rest of the instrument may then be cleaned without danger of any change taking place in the gas volume inclosed in the correction tube.

To prepare the apparatus for use, draw some distilled water through the capillary *g* into the correction tube *B*, and also moisten the walls of the measuring tube *A* with a drop or two of water. Fill the level-bulb *G* with mercury, and turn the glass stopcock to the position shown in *D*₁. Then by raising the level-bulb drive the mercury over into the manometer tube until the latter is filled up to the marks on *k* and *i*.

Before proceeding with the analysis, the volume of the manometer tube from the mark on *k* to the point *a* must be ascertained.

To do this, draw over the mercury in the manometer until it reaches *a*, then turn the stopcock *D* until it has the position of *D*₂, and now draw any desired volume of air into the burette. Leaving the stopcock open, read off this volume of air on the scale of the burette, the air here being, of course, under the prevailing pressure of the atmosphere. Turn stopcock *D* so that the burette communicates with the manometer tube, and drive the air over into this latter tube until the mercury in it stands at equal height in its two branches; that is, at the marks on *k* and *i*. The difference between the two readings on the measuring tube, provided the tube *g* remains open, gives the volume of the manometer from the mark on *k* up to *a*.

Correction tube *B* may be used in either of two ways. We may inclose within it an indeterminate amount of air by simply fusing together the end of the tube *g* so that the volume in the correction tube will correspond to the barometric pressure and temperature prevailing at the time of operation, or we may fill *B* with such an amount of air that the apparatus will indicate directly gas volumes reduced to standard conditions — that is, to 0° C. and 760 mm. pressure. In the latter case, the gas will have at the ordinary temperature of the room a pressure somewhat above that of the atmosphere. In the former case the barometer and the thermometer must be read at the time the tube *g* is fused together, so that we may be able to correct gas volumes whenever this is necessary.

In many cases it is highly desirable to so arrange the apparatus that the reading on the measuring tube *A* corresponds directly to volumes at 0° C. and 760 mm. pressure. To accomplish this a piece of rubber tubing is slipped over the end of the capillary tube *g* and fastened firmly in place by a wire ligature. By lowering the level-bulb, mercury is drawn over into the manometer tube until it reaches the capillary *l*, and the burette is then allowed to stand for two hours in a room of fairly constant temperature. The stopcock *D* is then opened so that the contents of the burette are in free communication with the

atmospheric air. As soon as one is convinced that all parts of the apparatus are at the same temperature, the gas volume in the burette is read exactly, and the temperature and barometric pressure are noted. The thermometer and barometer should stand in the same room with the apparatus. The stopcock *D* is closed and the volume which the gas would occupy at 0° C. and 760 mm. barometric pressure is now calculated.

Example. — The gas volume is 97 cc., the barometric pressure 753.3 mm., and the temperature 8.75° C. The space from *k* to *a* in the manometer has previously been determined and found to be 1.8 cc. The tension of the water vapor at 8.75° C. is 8.4 mm. The corrected volume is 92.1 cc.

Since, however, in making measurements with the correction tube, the gas fills the space from *k* to *a*, this volume must be subtracted from the above result: —

$$92.1 - 1.8 = 90.3 \text{ cc.}$$

In order now to adjust the gas volume in the correction tube so that readings of volumes in the burette will be reduced at once to standard conditions, the stopcock *D* is turned so that the burette communicates with the manometer tube, and the gas in the burette is compressed by raising the level-bulb *G* to the volume which it has been calculated that it would occupy at 0° C. and 760 mm. pressure. The mercury in the manometer tube is, of course, forced out of equilibrium by this operation. Air is now blown into the correction tube through the rubber tube at *g* until the mercury stands at the same height in the two branches of the manometer tube, and the rubber tube is then closed by means of a strong pinchcock placed directly above the end of *g*.

A rubber tube cannot remain tight for any length of time, and therefore the glass tube *g* must be fused together. This cannot be done at once because of the high pressure of the air in the correction tube, but the operation may easily be performed by first removing the rubber tube joining the manometer tube

with the burette at *a* and then placing the correction tube *B* in a freezing mixture of salt and ice, allowing it to stand therein until the mercury in the manometer shows that the pressure on the inside of the correction tube is smaller than that of the external atmosphere. The tube *g* can now be heated by means of a blast lamp and drawn out and fused together directly below the rubber tube which is upon it.

There is danger that the glass tube *g* may crack when it is heated. This can be avoided by painting it with a thin emulsion of Plaster of Paris stirred up with water, leaving the place where the tube is to be drawn out uncovered by this coating. The Plaster of Paris offers an excellent protection against the overheating of that part of the glass tube which it is not desired to soften and can afterward easily be removed with the aid of water.

The correction tube, after being thus adjusted, is again joined to the burette. The readings of gas volumes in the burette now give directly the volumes under standard conditions, no matter how great may be the variations of temperature and pressure, provided always that in making the measurements the stopcock is turned to the position of D_1 and the mercury in the manometer tube is brought to the marks *k* and *i* by expanding or compressing the gas in the measuring tube. The exact adjustment of the mercury in the manometer tube is effected by raising or lowering the level-bulb *G* until the mercury stands nearly at the marks *k* and *i*, then closing the stopcock *n* and turning the screw *o* so as to exert greater or less pressure on the piece of rubber tubing against which it plays. This piece of rubber tubing, as is shown in the figure, connects the lower end of the burette with the stopcock *n*. In this manner the surface of the mercury in the two arms of the manometer may be brought exactly to the same level. This style of adjustment is original with Pettersson and enables us to effect slight changes in the size of the gas volume in a most convenient and rapid manner. In all cases where rubber tubing must withstand considerable

pressure it is desirable to use enamelled rubber tubing which, although not quite as elastic as the ordinary kind, will easily withstand a pressure of several atmospheres.

II. The Absorption Pipettes

On account of the great differences in pressure caused by columns of mercury of only moderate height it becomes necessary

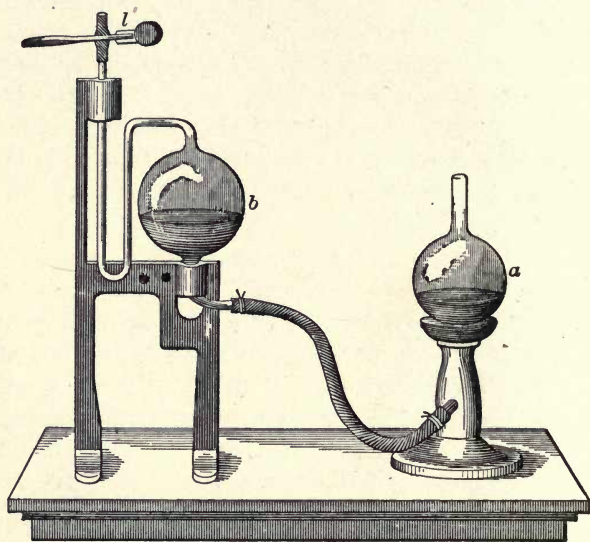


FIG. 50

to give to these absorption pipettes, which are partially filled with mercury, a form somewhat different from that adopted for the pipettes containing aqueous solutions.

The Simple Mercury Absorption Pipette

This consists of two bulbs, *a* and *b*, Fig. 50, joined together by a piece of enamelled rubber tubing. The bulb *a* has a capacity of about 130 cc. and *b* a capacity of about 150 cc.

The Simple Mercury Absorption Pipette for Solid and Liquid Reagents

This resembles the pipette just described, except that the bulb *b*, Fig. 51, is cylindrical in form and has at its lower extremity a cylindrical neck, *i*, through which the bulb can be filled with solid substances. *i* is then closed with a cork or rubber stopper held in place by a wire ligature.

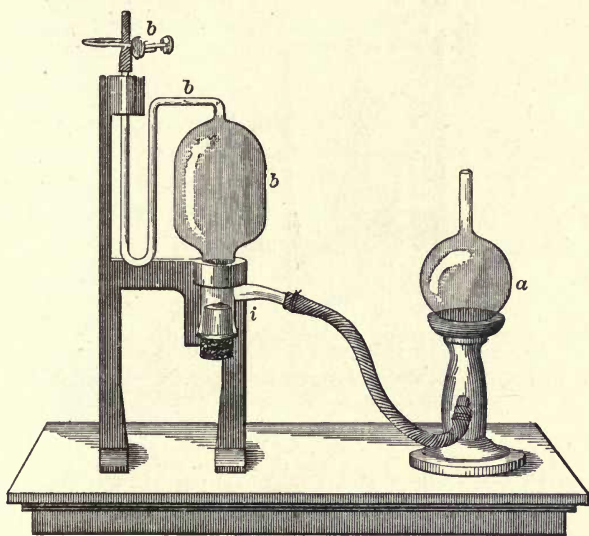


FIG. 51

The Mercury Absorption Pipette with Absorption Bulb

This pipette has in addition to the two bulbs *a* and *b*, Fig. 52, a third bulb *c* filled with broken glass or with glass beads. The advantage of this small bulb lies in the fact that when the gas is driven over into the pipette, the reagent which the latter contains clings to the small pieces of glass in *c*, and causes a

more complete absorption of that constituent of the gas mixture which is to be removed. The pipette has, however, one drawback: with viscous reagents bubbles of gas are liable to cling to the broken glass in *c*.

The mercury pipettes are manipulated in exactly the same manner as the pipettes for aqueous solutions above described, except that here only small quantities of the reagent are employed in order to reduce the error that is caused by the solu-

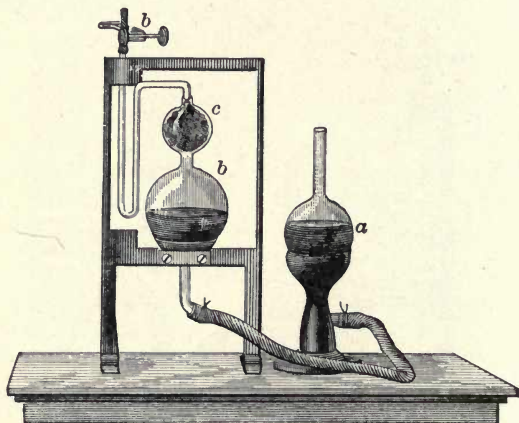


FIG. 52

bility in the reagent of those gases which are not directly absorbed by it. This error can be still further lessened by introducing into the gas pipette an amount of reagent sufficient for two analyses of the gas mixture in question. In the first analysis the reagent becomes saturated with those gases for which it is not an absorbent, and the error due to solution of the gases in the reagent is thus minimized in the second analysis. The reagents are introduced into the gas pipette by means of a small pipette inserted in the rubber tube *b*.

B. APPARATUS FOR EXACT GAS ANALYSIS WITHOUT RUBBER CONNECTIONS OR STOPCOCKS

Experience has shown that even the best glass stopcocks cannot be relied upon with certainty for any considerable length of time, and rubber connections will allow small quantities of gas gradually to pass through them. It is therefore apparent that an apparatus which contains no stopcocks or rubber connections whatever possesses decided advantages over one in which errors arising through leakage are liable to occur.

The wonderfully simple and exact gasometric methods devised by Bunsen fulfill completely these demands, but unfortunately the rapid performance of a large number of exact analyses is not possible with his apparatus.

The method devised by Doyère¹ resembles that of Bunsen, in that the analysis is carried out in glass vessels fused together, and all ground joints and rubber connections are avoided: it has, however, the fault that great accuracy can be obtained only by the use of very cumbersome apparatus.

By the introduction of a different manner of measuring and a somewhat changed construction of the necessary absorption pipettes, Hempel has endeavoured to improve the Doyère method, so that, in its changed form, rapid and very exact work may be possible without the use of delicate physical instruments.

Bunsen measures the gases under varying pressure and varying volume, and Doyère measures them under constant pressure and varying volume, while in the method about to be described the measurements are made under constant volume and varying pressure. Following Boyle's law, the values so found bear the same proportion to one another as do gas volumes under the same pressure.

¹ *Ann. chim. phys.* [3] 28, (1850), p. 1.

Doyère¹ measures the gases in a Bunsen eudiometer, and he avoids correction for pressure by joining the eudiometer with an iron holder having a screw attachment, by means of which the mercury in the tube and in the suitably formed trough may be brought to the same level. The readings are made with a special telescope of great exactness. The absorptions are effected in Doyère's improved Ettling gas pipette.

The manipulation of the pipettes demands that the eudiometer at some place in the mercury trough be brought wholly beneath the level of the mercury, and further, that the suction tubes of the pipettes be as long as the eudiometer. From these two particulars it results that when a very deep trough is used, the pipettes are very unwieldy and easily broken, or that when a shorter eudiometer is employed, a sharp reading of the scale can be made only with the most perfect instruments, since it must be possible to measure with exactness tenths of a millimeter.

Doyère states that the measuring tubes used by him have a length of 20 cm. and an internal diameter of 15 mm. For large gas volumes he uses vessels similar to those employed by Bunsen for this purpose, the lower part being cylindrical and graduated, and ending above in a bulb.

The method here to be described permits, by the employment of spherical measuring vessels, the use of a shallow mercury trough and of shorter, more easily manipulated, and less fragile gas pipettes, and a measurement more than three times as sharp, since with this apparatus, if the gas at the beginning of the analysis nearly fills the bulb at atmospheric pressure, the scale has an available length of 760 mm. while Doyère's measuring tube is only 200 mm. long.

The measurements are made at constant volume, varying temperature, and varying pressure. This is accomplished by placing the gas in small glass bulbs which can easily be brought into communication with the manometer tube, by then ex-

¹ *Loc. cit.*, also Fehling's *Handwörterbuch der Chemie*, vol. 1, p. 512.

panding the gas to a certain volume by lowering a movable vessel filled with mercury, and finally reading on the manometer tube the pressure under which the gas now stands. According to Boyle's law the values thus obtained bear the same proportion to one another as do gas volumes under the same pressure.

The absorptions are effected in gas pipettes to be described later.

THE MEASURING APPARATUS

This (Fig. 53) consists of an iron mercury trough *A* (on account of the presence of water, wood cannot be used, since it would swell and change form), of a glass tube *D* graduated in millimeters and from 76 to 80 cm. long and further, of the wooden stand *G* and the water reservoir *E*. The sides of the water reservoir *E* are glass panes, one of which *e* extends only so deep into the mercury as to leave room to bring the capillary of the pipette *B* under it into the measuring bulb *C*.

By placing the measuring bulb upon the rubber stopper *a* in the mercury trough it can always be brought, by means of the holder *f*, into mercury-tight connection with the graduated tube *D*. The tube *b* and the $\perp$ -piece *d* are made of iron. *D* is connected with an arm of *d* by means of a piece of enamelled rubber tubing, or ordinary rubber tubing so wrapped as to enable it to resist the pressure of the mercury. A piece of enamelled rubber tubing joins the other arm to the movable level-bulb *H*, but between *d* and *m* there is introduced the Pettersson device for the fine adjustment of the mercury. (See Fig. 106.)

In making the measurement, the measuring bulb *C* is brought into the position shown in Fig. 53, and is pressed down tightly upon the rubber stopper *a* by means of the clamp *f*. Mercury is then drawn out through *d* until the meniscus of the mercury in the measuring bulb lies nearly tangent to the horizontal hair of a magnifying glass which is fastened to the apparatus op-

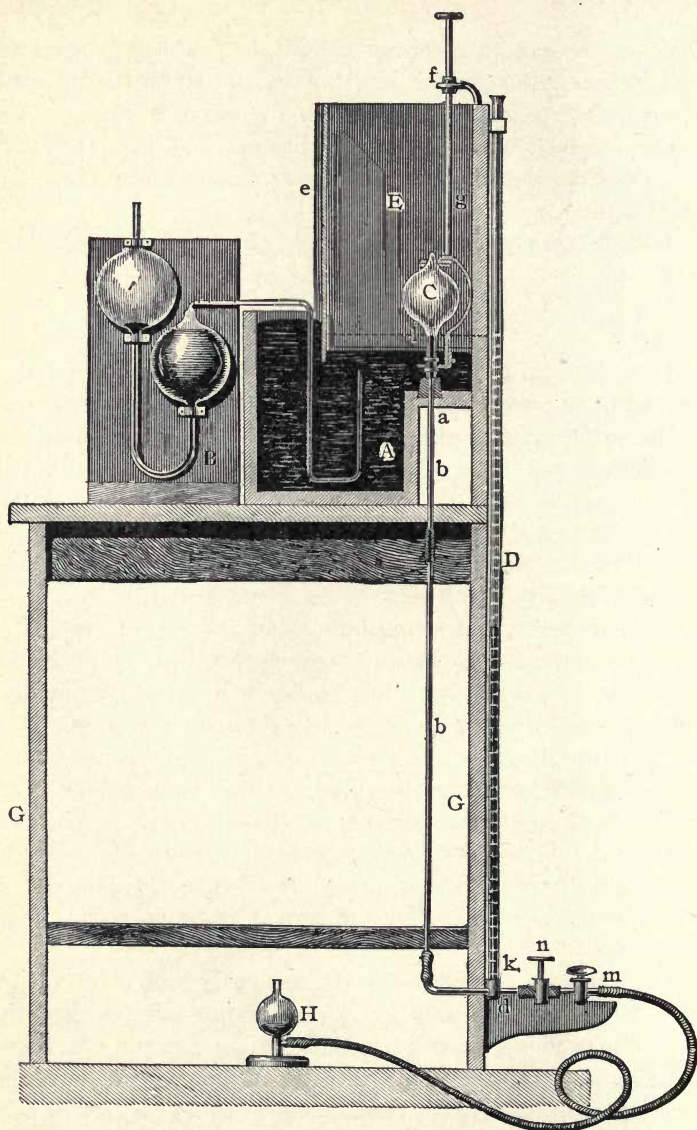


FIG. 53

posite l . This glass is not shown in the figure. m is then closed and the exact adjustment of the height of the mercury at l is effected by turning the screw n .

The height of the mercury in the manometer tube D is now read with a cathetometer, and the pressure of the gas in the bulb is then calculated.

Since the space in the bulb is kept saturated with water vapor by moisture in the bulb, the corrected pressure of the gas in the bulb is ascertained by use of the equation

$$P = b - m - d$$

in which b is the observed barometric pressure, m the pressure of water vapor at the temperature of the water in the reservoir E , and d the pressure in the manometer D .

THE MEASURING BULB

The measuring bulb E (Fig. 54) is fastened to the iron holder g by means of the projecting tubes r and s . r , which is closed at the top, is about 5 mm. long and s about 30 mm. At from 5 to 7 mm. below the bulb, s is widened into a collar x by softening the glass tube in the blast-lamp flame and pressing it together. The iron holder g has at t a thick perforated sheet-iron cap for holding r . The holder bends around the bulb and is supplied at the lower end with the perforated iron plate u , which is bent at a right angle, and holds the projection s . u may be set where desired by means of the screw v , to which the slot through which it passes gives a play of several millimeters. s projects 4 to 5 mm. beyond the plate u . The iron collar y is fastened to g in such a position that it just slips under the fork f when the holder and bulb are placed over the end of the iron tube passing through the rubber stopper m , and are firmly pressed against the rubber. The fork is firmly fastened to the slide i , which can be moved up and down by the screw h . By screwing the slide down, the measuring bulb can be pressed against the rub-

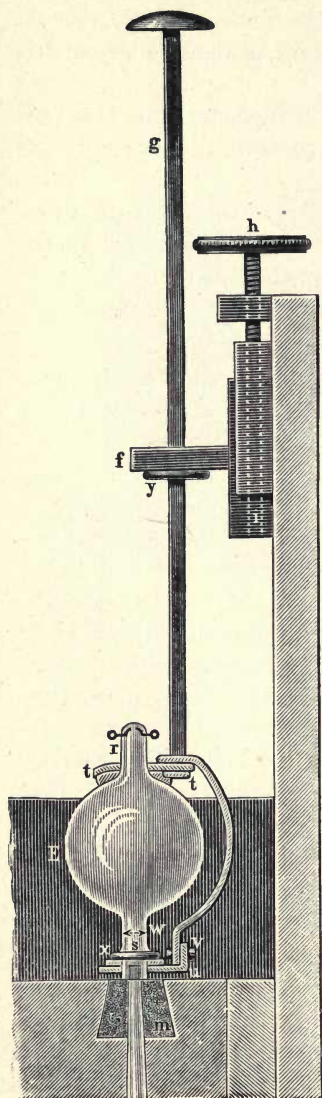


FIG. 54

ber stopper and a tight connection with the barometer tube thus be obtained. A scale upon the slide *i* and its guides makes it possible to bring the bulb at different times into exactly the same position as regards the millimeter scale of the barometer.

The total height of the measuring bulbs varies from 7.5 to 9.5 cm.

Since the walls of the measuring bulbs are only as thick as those of ordinary bulb pipettes, it was thought possible that, in the measurement of very small gas volumes, the volume of the bulb might be decidedly changed, since under such conditions it is exposed to nearly the full pressure of the atmosphere.

To settle this question, Hempel determined the volume of the bulb, first empty and then filled with gas, in a stereometer, and it was found that even with large bulbs of 100 cc. capacity no measurable difference of volume could be detected; hence even thin-walled glass bulbs may be used without hesitation for these measurements.

Curiously enough, it is quite

difficult to lower the measuring bulb through the water in *E* (Fig. 53) down into the mercury below without some water getting into the inside of the bulb. If this should happen, exact reading would, of course, be impossible. The operation can be performed, however, by bringing the measuring bulb into two porcelain crucibles placed one within the other in the manner shown in Fig. 55, and then filling these two crucibles with mercury. When these are lowered through the water into the mercury the larger crucible *A* is first removed, and then the crucible *B* is lowered away from the mouth of the

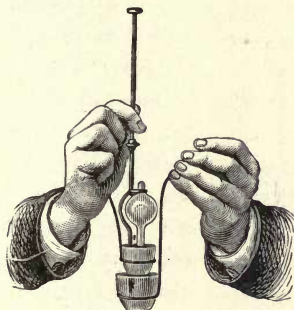


FIG. 55



FIG. 56

bulb. The opening in the bulb is now below the surface of the mercury, and yet no water has entered it.

By means of the instrument shown in Fig. 56 the air may be sucked out of the measuring bulb, and the gas sample can then be transferred to the bulb by means of one of the pipettes described below.

GAS PIPETTES FOR LIQUID ABSORBENTS

The gas pipettes were devised by Ettling and were first used by Doyère as absorption vessels for gas analysis.

They consist of two bulbs *a* and *b* (Fig. 57), of the same size, joined together by the tube *c* and ending in the bent capillary tube *d*. A very small bore thermometer tube, and not a tube

of 1 mm. bore as Doyère suggests, is used as the capillary, thus making it easy to avoid introducing absorbent into the measuring bulb or leaving any considerable quantity of gas in the pipette.

Gases move rapidly in capillary tubes, but liquids, especially concentrated solutions of salts, move very slowly; hence it is easily possible to bring the gas residue in the pipette to less than $\frac{1}{1000}$ of a cubic centimeter without danger of the absorbent en-

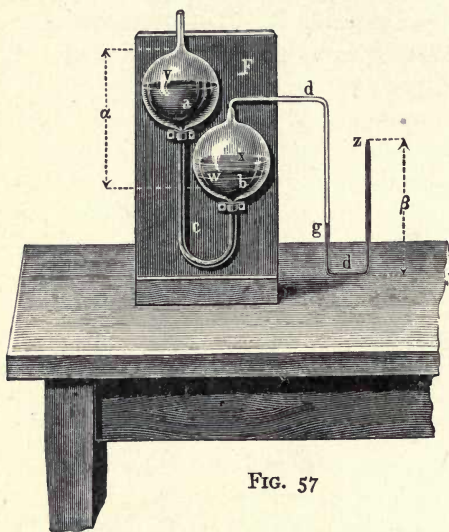


FIG. 57

tering the measuring bulb. It is almost impossible to do this when wider glass tubes are used.

The pipettes must be so made that the distance a (Fig. 57) is only as large as or smaller than β : the capillary must be bent close to the bulb b . The pipettes are fastened to the wooden standard in such a position that the capillary d comes to within a few

millimeters of the bottom of the mercury trough when the pipette is placed in the position shown in Fig. 53.

The bulbs of the pipettes must be considerably larger than the volume of the gas to be brought into them. The inconvenience of carefully cleaning the pipette after the absorption is avoided by using a special pipette for each reagent. Pipettes of very different sizes are employed, the sizes depending naturally upon the dimensions of the measuring bulbs.

To bring a measured amount of the absorbent into the pipette, which is first filled with mercury, connect it by means of

a piece of rubber tubing *e* (Fig. 39) with the small burette *f* containing the reagent and supported by the clamp *g*. Open the pinchcock *h*, slip a rubber tube over the burette at *i*, and by suction so exhaust the air in the burette that any gas remaining in the pipette will be drawn through the capillary *x* and through the absorbent. The pipette is thus completely filled with mercury. Stop the suction as soon as the mercury is visible above the rubber *e*, put the rubber tube on the pipette at *l*, and draw the mercury back to the capillary. Note the height of the absorbent in the burette, and then suck the desired amount of the same through the capillary *d* into the pipette. At the moment when the necessary amount of reagent has passed over, bring a drop of mercury into the burette at *i*.

The amount of the absorbent introduced may be sharply determined by drawing the mercury into the pipette until the reagent is again visible in the capillary *d*, and then noting the height of the reagent in the burette.

The bent capillary tube of the pipette is cleaned and freed from all traces of reagent by lowering the tube into a beaker filled with distilled water, and then drawing water into the capillary and driving it out again by sucking and blowing on a rubber tube attached to the open end of *a*.

The pipette thus prepared for the analysis contains mercury between *v* and *w*, between *w* and *x* the absorbent, and from *x* to *y* mercury (Fig. 39).

GAS PIPETTES FOR SOLID ABSORBENTS

To bring the gases under examination into contact with solid absorbents,

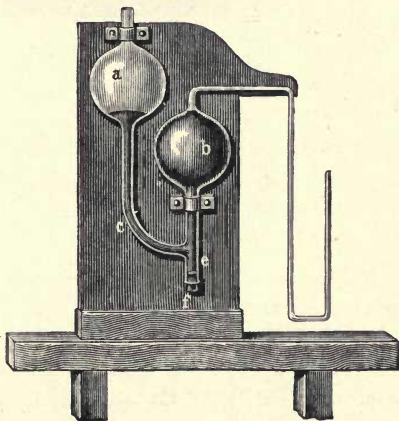


FIG. 58

the form of pipette shown in Fig. 58 is used. In this the tube *c* has a branch tube *e* through which solid substances, such as sticks of phosphorus, are introduced into the bulb *b*;

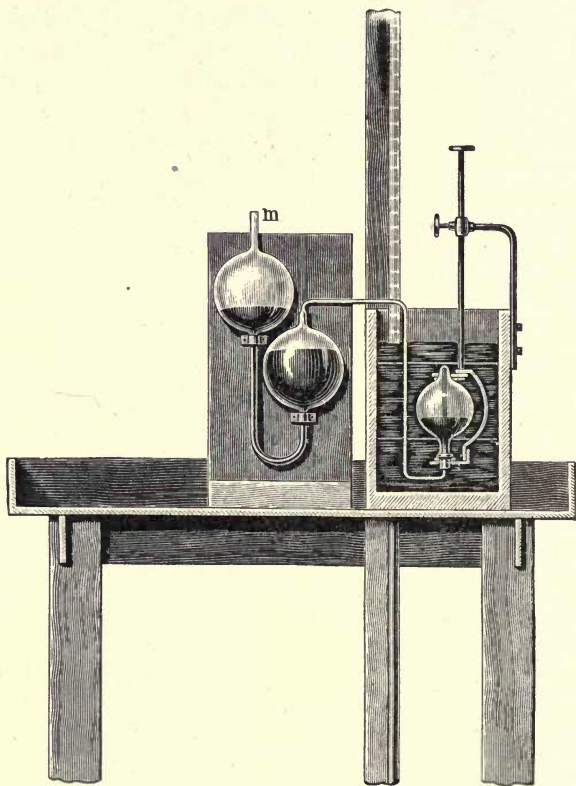


FIG. 59

e is then closed at *f* with a cork, and the pipette is filled as usual with mercury. When a gas is drawn in, the solid substances remain in the bulb *b*, and so come into contact with the gas.

THE ABSORPTION

The gas pipettes already described are used for the absorptions, the manipulation being shown in Fig. 59 and Fig. 60.

Figure 59 gives the position in which it is possible to bring the gas completely into the pipette. The measuring bulb is here brought below the surface of the mercury and the gas is drawn into the pipette by sucking with the mouth on a rubber tube attached to *m*. The suction is discontinued at the moment when the mercury begins to flow from the capillary into the bulb of the pipette.

The pipette then contains (see Fig. 57) mercury from *v* to *w*, absorbent from *w* to *x*, gas from *x* to *g*, and mercury from *g* to *z*, so that the pipette, after it is taken out of the mercury trough, may be vigorously shaken and a rapid absorption effected.

To drive the gas from the pipette back again into the measuring bulb, the apparatus is brought into the position shown in Fig. 60.

In the beginning it is necessary to blow into the pipette at *m* to set the gas in motion; when it has once started, the mercury in the measuring bulb acts with an aspirating effect, so that the gas passes over of itself. At the moment when the absorbent has risen to about 1 cm. from the end of the capillary in the measuring bulb, the capillary is lowered under the mercury, and mercury is drawn into the capillary by sucking on the rubber tube attached to *m*. In this manner the entering of reagent into the measuring bulb may be avoided with certainty.

If a gas thread about 1 cm. long remains in the capillary, this corresponds to approximately 0.001 cc. of gas, since the total 35 cm. length of the capillary has a volume, determined by weighing the mercury which it holds, of 0.038 cc. Consequently no appreciable error arises from this source.

The analysis is made as follows: —

Fill the carefully cleaned and moistened measuring bulb with the gas under examination by lowering the bulb into the mercury in the trough, drawing out the air in it with a gas

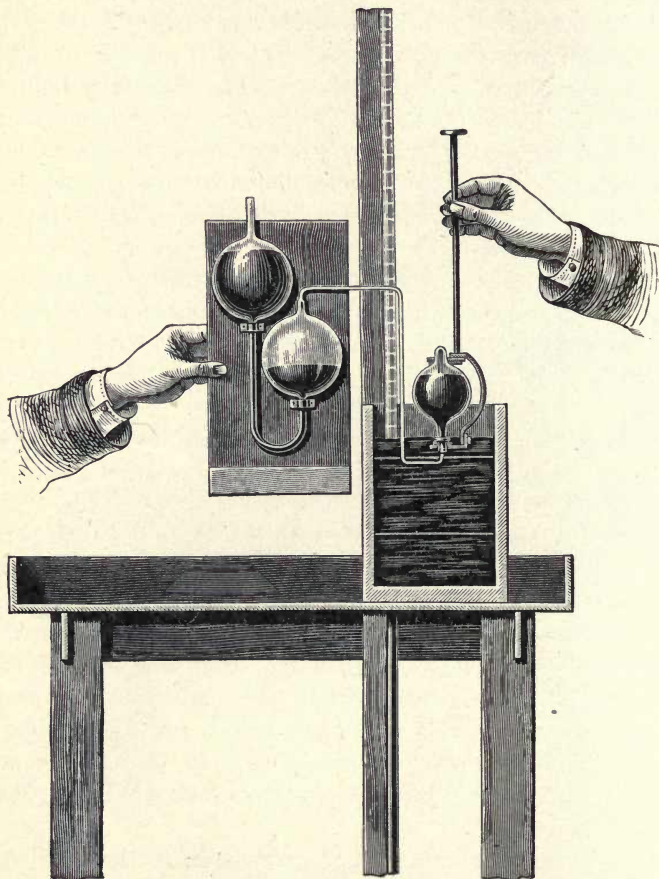


FIG. 60

pipette, and bringing the gas into the bulb either by means of a delivery tube brought under the mouth of the bulb or by means of a gas pipette.

The necessary measurements, absorptions, and explosions now follow, their order being determined by the nature of the gas.

Since difficulties arise only in the use of fuming sulphuric acid over mercury, while all other reagents can easily be manipulated in the manner already described, the reader is referred to Chapter XIII for descriptions of methods of absorption of the various gases.

The heavy hydrocarbons cannot be absorbed with fuming sulphuric acid in the manner described, because, on bringing together the fuming acid and mercury, sulphur dioxide is evolved even in the cold, and acid sulphates are formed which, upon long standing, separate as thick crusts and obstruct the pipette. Since, however, the gases that are not absorbable by the fuming acid are very insoluble in the same, a pipette completely filled with the acid may be used, the mercury here coming into contact with the sulphuric acid only in the capillary tube. If care be taken in the manipulation that no mercury passes over from the trough into the pipette, and if, after using, all mercury be removed from the capillary by means of a common suction pipette attached thereto, so that sulphuric acid alone remains in the pipette, a stoppage of the capillary, which, when it has once taken place, is difficult of removal, need not be feared.

To protect the lungs from the fumes of the sulphuric acid, a glass tube filled with pieces of caustic potash is interposed between the rubber suction tube and the pipette.

Unless very accurate results are desired, it is sufficient to make all readings with the unaided eye, for if the eye be brought only approximately to the same plane with the surface of the mercury column that is to be read, the results thus obtained are quite close to the truth.

The accuracy of the analysis may easily be greatly increased by using a number of measuring bulbs of different sizes and determining their volumes by filling them with mercury and weighing the mercury. The gas to be analyzed is then first

brought into the largest bulb and one or more of its constituents are determined. If the remaining volume now amounts to only a half or two-thirds of the original volume, this residue is introduced into a smaller measuring bulb. This procedure permits of the use of the total length of the manometer tube *D* (Fig. 53) in making the measurements, and consequently insures much greater accuracy in the readings.

CHAPTER VIII

THE CONSTRUCTION AND CONNECTION OF APPARATUS

Glass Blowing. — It is of great convenience to the gas analyst to be able to make simple forms of glass apparatus and to repair broken parts. The elements of glass blowing are clearly described in such books as that by Shenstone, and with practice it is possible for almost every chemist to develop considerable facility in glass blowing.

The blast-lamp should have cocks on the lamp itself for the easy regulation of the supply of gas and air blast. It should give with full blast pressure a colorless flame about thirty cm. long, and with diminished blast pressure a yellow-tipped flame about forty cm. long. On cutting down the gas and air pressure, the lamp should furnish a small, sharp pointed, colorless flame about five cm. long.

The glass tubing should be easily fusible and the ordinary sizes, from six mm. to twenty mm. in diameter, should have a wall about one mm. thick. Glass tubes or glass parts that are to be fused together should be of the same kind of glass, for joints made of different kinds of glass will usually easily break apart. All joints should be highly heated and thoroughly blown out, and should be carefully annealed by holding them in the luminous flame of the lamp until they are thoroughly coated with soot and then allowing them to stand until cold.

Amateurs that have difficulty in blowing glass bulbs in the middle of tubes will find it convenient to order from a glass manufacturer a supply of thin walled glass bulbs, of from four cm. to seven cm. in diameter, with side tubes of from seven mm. to twelve mm. external diameter and each about fifteen cm. long.

Since some find difficulty in properly bending capillary tubing for the Hempel apparatus it may be stated that such tubing, which should be six mm. external diameter with one mm. bore, may easily be bent, without blowing, by first warming it carefully in the luminous flame of the blast lamp, and then heating the spot at which the bend is to be made in a blast flame about two cm. wide, turning the tubing during the heating. As soon as the tube softens, it is bent directly to the desired angle as one would bend a piece of glass rod.

Mounting of Apparatus.—If glass apparatus is to be mounted on a frame or standard, it should be fastened at only a few places so as to allow of as free expansion as possible, and it is best secured in position by fastening to the support a metal band that passes around the glass tube, but does not touch it, and then filling the intervening space between the metal strap and the tube with Plaster of Paris.

Rubber Connections.—If glass tubes are to be joined together by rubber tubing, the ends of the tubes should be rounded in the flame, and should be brought close together within the piece of rubber tubing. To secure the rubber tubing in place, it may be fastened by wire ligatures. For this purpose copper wire about one mm. in diameter is most suitable. Each ligature should consist of only one turn of the copper wire around the tube, the ends being drawn and tightly twisted together by means of a pair of pliers. Long rubber connections should be avoided, not merely because the rubber tubing is somewhat porous, but also because air in the tube adheres tenaciously to the walls. A rubber tube capable of withstanding high pressure is needed in connecting level-tubes or level-bulbs with gas burettes when the apparatus is to be filled with mercury as the confining liquid. For this purpose the so-called enamelled rubber tubing about six mm. internal diameter and with a wall two mm. thick will be found very satisfactory. For connecting the level-bulb of a mercury air pump with the pump, enamelled rubber tubing about twelve mm. internal diameter and 2.5 mm. thickness of

wall may be employed. The enamelled tubing is superior to the ordinary pressure rubber tubing with very thick wall, because its larger internal diameter permits free flow of the mercury, and its smooth interior surface avoids the fouling of the mercury by particles of the rubber. It has been found in practice that it will easily withstand a working pressure that rises at times to five atmospheres.

Stopcocks. — Hollow-blown stopcocks are so perfectly made that they may be employed with very slight danger of leakage



FIG. 61

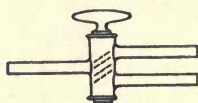


FIG. 62

provided they are properly lubricated. The Greiner & Friedrichs form of stopcock of the form shown in Fig. 61 and Fig. 62 is superior to the stopcock with straight bore because it avoids the danger of leakage due to the channeling of the barrel of the stopcock.

Lubrication of Stopcocks. — An excellent preparation for the lubrication of glass stopcocks that does not deteriorate on keeping, does not work out at the ends of the key, and gives off no hydrocarbon vapors may be made as follows: Place in an evaporating dish twelve parts of vaseline and one part of paraffin wax. Heat this mixture over a Bunsen flame and maintain the contents of the dish at a temperature that will keep the materials fluid but will not cause the mixture to emit fumes. Drop in successive portions of soft, black-rubber clippings and stir the mixture after each addition until the rubber is completely dissolved. After about nine parts by weight of rubber has been added, take out a small sample of the lubricant on the end of a stirring rod, allow it to cool, place it on the ball of the thumb, squeeze it with the end of the middle finger and then rapidly tap the finger upon the thumb at the point covered

by the lubricant. If on this treatment the lubricant forms light feathery particles that float off in the air in fine flocks the proper mixture has been reached. If the lubricant does not behave as described, stir in more rubber and test again. About ten parts by weight of the rubber will usually be required for the above amounts of vaseline and paraffin.

In lubricating a glass stopcock, the key and barrel should first carefully be cleaned and then the thinnest possible film of vaseline be rubbed over the surface of the key of the stopcock. The lubricant is then rubbed over the key which is next inserted in the barrel and turned around until the lubricant is evenly distributed over the surface.

In the Cornell laboratory, it has been found that a Greiner & Friedrichs stopcock of the form shown in Fig. 61, when lubricated with this mixture, will withstand a pressure of four atmospheres on one side and a Torricellian vacuum on the other for a considerable length of time without any leakage whatsoever.

Another recipe for a lubricant for stopcocks is given by Keyes:¹ 26 grams of paraffin (melting point 70°) is placed in a dish and heated until it melts, and then 18 grams of pure gutta percha is added in small amounts at a time, the temperature of the mass being held at about 150° until the gutta percha is dissolved. 20 grams of a heavy mineral oil such as is supplied with the Fleuss pumps is then added and the mixture is maintained at a temperature of from 125° to 130° for four or five hours.

If the gases or liquids that are to pass through the stopcock are of such nature as to cause them to attack the rubber lubricant, metaphosphoric acid may be used. The key and barrel of the stopcock are thoroughly cleaned and dried; the key is dipped into phosphorus pentoxide, is allowed to stand in the air until the pentoxide has taken up sufficient water to form metaphosphoric acid, and is then inserted into the barrel and turned until the metaphosphoric acid is spread evenly over the surface.

¹ *J. Am. Chem. Soc.*, 31 (1909), 1271.

CHAPTER IX

PURIFICATION OF MERCURY

Mercury that is pure will pass over a glass surface without adhering to it or leaving a deposit upon it. If the mercury is contaminated with other metals there forms upon the mercury a layer of oxides that adhere to glass. Commercial mercury frequently contains zinc and lead, and through use in the laboratory it usually soon becomes contaminated with copper. These foreign metals may be removed by oxidizing them and then dissolving their oxides with an acid that does not attack the mercury. They may also be separated from the mercury by bringing the impure metal into contact with a mercurous salt and a free acid, which will remove from the mercury such metals as stand above it in the electromotive series, the foreign metals passing into the solution and precipitating an equivalent amount of mercury. Metals that stand below mercury in the electromotive series, such as platinum and gold, cannot be separated from the mercury in this manner. In such case it is best to distill the mercury under diminished pressure. It was formerly supposed that certain metals, such as zinc, would distill over with the mercury, but Hulett has shown¹ that this does not take place if bumping of the mercury during distillation is avoided. He has ascertained, however, that when the mercury is contaminated with dry metallic oxides, these oxides may be carried over with the mercury vapor.

If the mercury is very impure a considerable portion of the dirt and oxides may be removed by running the mercury through a dry filter paper that is folded and placed in a glass funnel in the usual manner after the tip of the filter has been cut off.

¹ *Z. physikalische Chemie*, 33 (1900), 611.

The hole in the end of the filter paper should be from one to two mm. in diameter. The metal may then be purified by one of the processes described below.

Purification of Mercury by Nitric Acid.

— If the mercury is highly contaminated with other metals it may rapidly be freed from a considerable portion of these metals by placing it in a bottle, covering it with a layer of a five per cent solution of nitric acid, and blowing air through the mercury through a glass tube. If air blast is not available, the mercury and acid may be placed in a filtering flask into the neck of which is inserted a one-hole stopper carrying a glass tube reaching nearly to the bottom of the flask. Upon connecting the side arm of the flask with a suction pump, air will be drawn down through the tube and will pass upward through the mercury.

Further purification of the mercury by means of nitric acid may then be effected by use of the apparatus shown in Fig. 63.

A is a glass tube one meter long, from 2 to 3 cm. wide, and fitted at the lower end with a cork and the bent glass tube *D*. *B* is the supply bottle for impure mercury, and *C* the receiver for the purified mercury. The lower end of the tube from *B* is drawn down to a

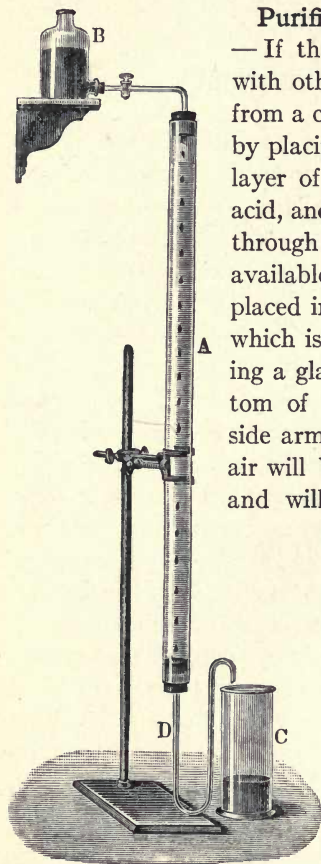


FIG. 63

small opening. Some pure mercury is first poured into the tube *D*, and *A* is then filled with 5 per cent nitric acid, the acid being kept in the tube by the mercury in *D*. Upon allow-

ing the mercury to drop from *B*, the purified metal passes slowly over into *C*.

Purification of Mercury by Concentrated Sulphuric Acid and Mercurous Sulphate. — This is a very simple and efficient method which yields mercury that is both dry and of high purity.

The process of purification may conveniently be carried out in a heavy separatory funnel of from 2 to 4 liters capacity, the funnel being supported in a wooden stand at such a height that an ordinary bottle or beaker may readily be brought under its lower end. The funnel is first partly filled with mercury (impure mercury may be used here, if no purified mercury is at hand), and then about 500 cc. of concentrated sulphuric acid is poured upon the mercury and from 25 to 50 grams of mercurous sulphate is added. In the top of the separatory funnel is placed an ordinary funnel, the stem of which is drawn out to small diameter and turned upward. The mercury to be purified is poured into this latter funnel and flows slowly and in the form of a fine spray out of the end of the stem. It is freed from foreign metals that stand above it in the electromotive series by the action of the sulphuric acid and mercurous sulphate, and is thoroughly dried by passing through the concentrated acid, so that pure and dry mercury may at any time be drawn off from the separatory funnel. In starting the process, impure mercury which may first have been put into the funnel should, of course, be drawn off and run through the purifier a second time. The mercury in the separatory funnel should never be drawn down until it is near the stopcock, for some sulphuric acid might be drawn off with it.

Purification of Mercury by Distillation. — This method, as stated above, gives satisfactory results if the mercury is free from oxides and if bumping of the liquid during distillation is avoided. If foreign oxides are present, they should first be removed by one of the methods described above.

Of the many forms of apparatus that have been suggested

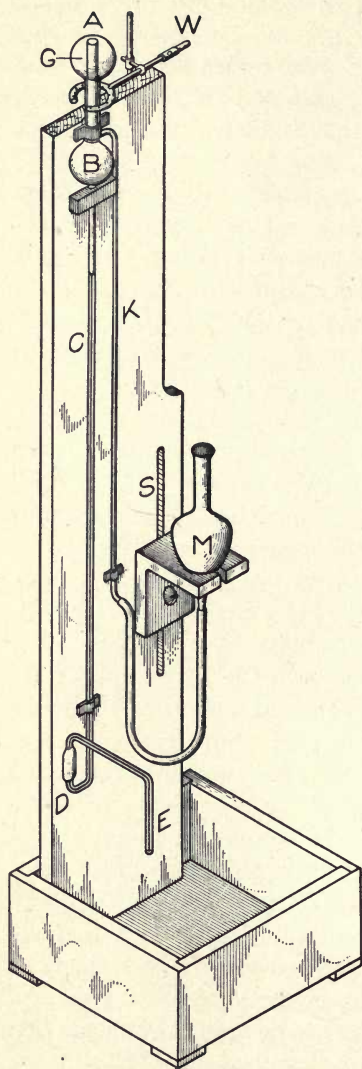


FIG. 64

for the distillation of mercury that shown in Fig. 64 is one of the simplest and most satisfactory. All glass parts of the device are of Jena glass. The mercury is boiled in the bulb *A* which has a diameter of about 7 cm. The neck of the bulb *A* is fused to the outside of the tube *G* just above *B*, and has a side arm *K* that is connected with the level-bulb *M* by a piece of enamelled rubber tube. To the lower side of the bulb *B* is attached a tube of 5 mm. internal diameter, and 15 cm. long, and to this is fused the capillary tube *C* that has a bore of about one mm. diameter, and a length of about 800 mm. The lower end of *C* is bent upward and widened at *D*, and then is brought up over the middle of the box and turned downward at *E*.

To start the distillation, dry mercury that has been freed from oxides is poured into the level-bulb *M*, and the capillary tube *E* is connected with a mercury pump or with an efficient water suction pump if a mercury pump is not available. *M* is then raised

until the mercury rises in *A* nearly to the top of the tube *G*, and the pumping is continued until all the air possible has been drawn out of *B* through *C*. *M* is then slipped into its adjustable support, and this is set at such a height in the slot *S* by means of a set screw that the bulb *A* is about half filled with mercury. The ring burner *W* is now lighted and the mercury carefully brought to boiling. The height of the level-bulb *M* is readjusted so that the bulb *A* stands half full of mercury. The vapor of the mercury passes from *A* down through *G* into *B*, and escapes through the open end of the capillary *E* into a container placed below *E* to receive it.

CHAPTER X

ABSORPTION APPARATUS FOR USE WITH LARGE VOLUMES OF GAS

Gases that are very soluble in water or that are present in only small amount in a mixture of gases are best determined by passing the gas mixture through suitable absorption apparatus to remove these constituents and then ascertaining the quantity of the absorbed gas by gravimetric or volumetric methods. The total volume of the gas mixture that is passed through the absorption apparatus is measured by a suitable device, such as an experimental gas meter. The meter is placed before the absorption apparatus if the gas that is to be determined is not appreciably soluble in water. Otherwise it is placed after the absorbent.

This method of analysis is particularly well adapted to the determination of minute amounts of a gas in a gas mixture for the reason that the large size of the sample that may here be employed renders the results very accurate if the absorbed constituent is correctly determined. To illustrate how slight is the effect, upon the final result, of a considerable error in the measurement of the sample, let us suppose that, in the determination of carbon dioxide in air, a sample of ten liters has been passed through the apparatus and the titration shows four cc. of carbon dioxide, or 0.04 per cent. If a mistake of 100 cc. were made in the measurement of the sample, which would be a very large experimental error, the result calculated for 10100 cc. would be 0.0396 per cent carbon dioxide, and for 9900 cc., 0.0404 per cent. To obtain the same accuracy by the volumetric analysis of a sample of air measuring 100 cc. the readings would have to be correct to the hundredth of a cubic centimeter.

To effect the complete absorption of a gas by a liquid, it is necessary that the gas be broken up into fine bubbles before or while passing through the absorbent, or that it remain in contact with the liquid for a considerable length of time. The former procedure, being more rapid, is usually to be preferred, and in the most efficient forms of absorption apparatus the gas enters the absorbent through small orifices in the inlet tube, or passes upward through a column of glass beads or of pieces of broken glass that are moistened with the absorbent. Many forms of the first type of absorption apparatus have been described and most of them are doubtless familiar to the reader. Special forms of such apparatus are pictured on pages 228 and 359.

A novel form of gas washing bottle that has been thoroughly tested in the Cornell laboratory and found to be very efficient is shown in Fig. 65. It is a slight modification of the spiral gas washing bottle recently designed by Fritz Friedrichs and placed upon the market by Greiner and Friedrichs. In preparing the bottle for use the stopper with the attached inner cylinder is removed, and the absorbing liquid is introduced into the outer cylinder in such amount that when the inner cylinder is replaced the liquid will stand at the height of the lowest spiral. The gas enters the bottle at *A* and passes into the absorbing liquid through small openings in the bottom of the inner cylinder. It cannot escape directly upward, but must pass around the spirals, which it does in the form of a procession of gas bubbles that push ahead of them small amounts of the absorbing liquid. The contact between the gas and the absorbent is intimate and of considerable

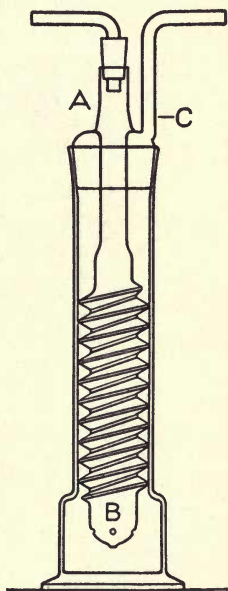


FIG. 65

duration, and the consequent absorption is very complete. This form of the bottle was particularly designed for quantitative work. Upon removal of the small rubber stopper that is inserted in *A* the absorbing liquid in the bottle can easily be removed, and the bottle be thoroughly rinsed out. If, however, the nature of the work is such as to render undesirable the use of a rubber stopper in *A*, the tube *A* may be made somewhat longer and bent at a right angle, Fig. 66, which will permit of a glass-to-glass connection of the apparatus.

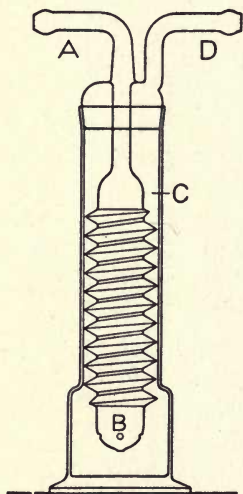


FIG. 66

If it is desired merely to remove a gas from a gas mixture, but not afterward to determine its amount, the apparatus devised by Winkler may be used. The device, Fig. 67, consists of a Wolff bottle *b* into one neck of which is inserted the stem of the cylinder *a*. To obtain large surface of contact between the absorbent and the gas, *a* is filled with pieces of pumice-stone. The gas enters through the tube *c* which extends downward to the bottom of the largest cylindrical portion of *a*. It then rises through the moistened pumice-stone and passes out through the tube *e*. The bottle *b* contains the absorbing liquid which can be driven up into *a* from time to time by blowing into the glass tube *d*, the excess

of absorbent immediately flowing back into *b* when the pressure at *d* is released.

In this Winkler absorption apparatus, however, the gas that rises through the cylinder *a* comes in contact with only such portion of the absorbent as adheres to the surface of the pumice-stone. Moreover if a large amount of gas is being removed by the absorbent the liquid must frequently be driven up into *a* by blowing into *d*. A modification of the apparatus that gives

more efficient absorption and automatically renews the absorbent is shown in Fig. 68. A Friedrichs spiral absorption tube fits by a ground joint into one neck of a Wolff bottle that contains the solution of the absorbent. Into the other neck of the Wolff bottle is inserted by means of a ground joint a

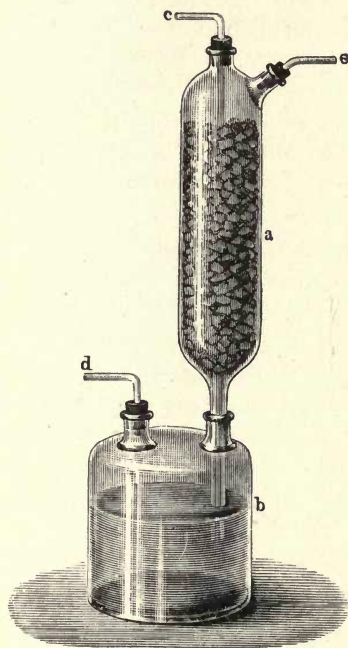


FIG. 67

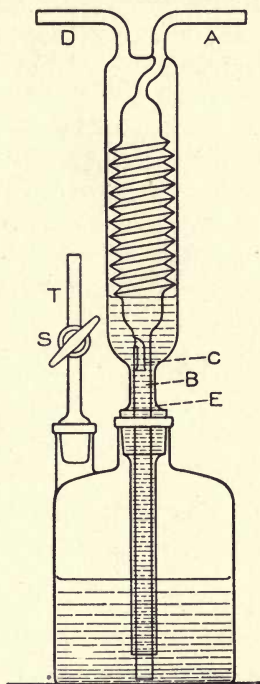


FIG. 68

short glass tube *T* carrying the stopcock *S*. Some of the reagent is driven up into the absorbing cylinder by opening *S* and blowing into *T* whereupon *S* is closed. The gas mixture enters through the tube *A* and, passing downward in the inside of the spiral, it enters the tube *B* and passes upward through the open lower end of the short tube *C*. It then rises

around the spiral carrying some of the liquid with it, and the non-absorbed gases escape at *D*. As the gas bubbles rise through the short tube *C* they draw up fresh absorbent through the tube *B* and the absorbent that has been in contact with the gas flows downward through the tube *E* into the Wolff bottle below. In this manner constant circulation of the absorbing liquid is attained and the apparatus requires no further attention after once it has been set in action.

CHAPTER XI

THE COMBUSTION OF GASES

Most gases may quantitatively be removed by absorbents, and for this reason the combustion method is chiefly employed for the determination of only hydrogen, methane and its homologues, and at times carbon monoxide. Under certain conditions, however, it may be advisable to determine the amounts of other constituents of a gas mixture by direct combustion even although these gases may be absorbable by suitable reagents. It is not always possible to ascertain from the results of a single combustion the percentage of each constituent in the gas mixture. De Voldere and de Smet ¹ have developed certain fundamental laws which show the possibilities and limitations of the combustion method, and the following condensation and revision of their original article has been prepared by Dr. R. P. Anderson.

According to de Voldere and de Smet the gases that may accurately be determined by combustion analysis are divisible into three classes:

I. Hydrocarbons.

$C_nH_{2n} + 2k$, where $k = 1, 0, -1, -2$, or -3 . It is convenient to include under this head CO , CO_2 , O_2 , and H_2 because the combustion equations of these gases are of the same type as those of the hydrocarbons, as is evident if the proper values are given to n and k . For example,

if $n = 0$ and	$k = 1$	$C_nH_{2n} + 2k$ becomes	C_0H_2 ,	equivalent to	H_2
" $n = 1$ "	" $k = -2$ "	"	" C_1H_{-2} ,	"	" CO
" $n = 0$ "	" $k = -2$ "	"	" C_0H_{-4} ,	"	" O_2
" $n = 1$ "	" $k = -3$ "	"	" C_1H_{-4} ,	"	" CO_2

¹ *Die Analyse brennbarer Gase, Z. f. analyt. Chem.*, 49 (1910), 661-688.

II. Gases containing carbon, hydrogen and oxygen.

Formic aldehyde, CH_2O ; methyl ether, $(\text{CH}_3)_2\text{O}$; methyl ethyl ether, $(\text{CH}_3\text{C}_2\text{H}_5)\text{O}$; ethyl ether, $(\text{C}_2\text{H}_5)_2\text{O}$; acetaldehyde, $\text{C}_2\text{H}_4\text{O}$.

III. Gases containing nitrogen.

Nitrogen, N_2 ; nitrous oxide, N_2O ; ammonia, NH_3 ; hydrogen cyanide, HCN .

Other combustible gases such as the hydrides of the fifth and sixth groups of the Mendeléeff periodic arrangement, halogen and sulphur hydrocarbon substitution products, and gaseous compounds of nitrogen other than those given above, yield combustion products that are not suited to gas-volumetric determination. The following discussion is confined to combinations of gases of the first class, finally amplified to include nitrogen or one of the other nitrogen-containing gases. For details concerning the combustion of gas mixtures containing members of all three of the above classes, the reader is referred to the original article.

In the combustion of a hydrocarbon four factors are determinable. These factors together with the symbols that will here be used to represent them are as follows:

V, the total volume of gas to be burned;

O₂, the volume of oxygen necessary for the complete combustion of the gas;

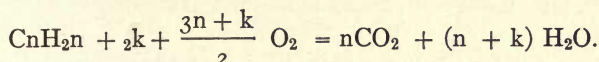
CO₂, the volume of carbon dioxide that is formed in the combustion;

T. C., the total contraction in volume that results from the combustion.

This total contraction is equal to the sum of the volume of the hydrocarbon and of that of the oxygen used, less the volume of carbon dioxide that is formed. The water that is produced in the combustion condenses to the liquid state.

$$\text{T. C.} = \text{V} + \text{O}_2 - \text{CO}_2. \quad (1)$$

The complete combustion of a hydrocarbon, C_nH_{2n+2k} , may be expressed by the equation —



In this case:

$$O_2 = \frac{3n+k}{2} V \quad (2)$$

$$CO_2 = nV \quad (3)$$

$$T. C. = \frac{2+n+k}{2} V \quad (4)$$

The following table gives the values of O_2 , CO_2 , and $T. C.$ per unit volume of hydrocarbons of the various groups.

TABLE I

k	GROUP	O_2	CO_2	T. C.	EXAMPLES
1	C_nH_{2n+2k}	$\frac{3n+1}{2}$	n	$\frac{n+3}{2}$	$CH_4, C_2H_6, C_3H_8, H_2$
0	C_nH_{2n}	$\frac{3n}{2}$	n	$\frac{n+2}{2}$	C_2H_4
-1	C_nH_{2n-2}	$\frac{3n-1}{2}$	n	$\frac{n+1}{2}$	C_2H_2
-2	C_nH_{2n-4}	$\frac{3n-2}{2}$	n	$\frac{n}{2}$	CO, O_2
-3	C_nH_{2n-6}	$\frac{3n-3}{2}$	n	$\frac{n-1}{2}$	CO_2

The four factors, V , O_2 , CO_2 , and $T. C.$ can also be determined in the combustion of any mixture of hydrocarbons, and by means of equations expressing the relationships between these four factors and the unknown volumes of the gases that are present, the volumes can, in certain cases, be computed. A study of these

equations shows that the number of gases that can be determined depends upon the nature of the gas mixture. The different possibilities are discussed under the following cases:

FIRST CASE. It is possible, by means of one complete combustion, to determine the percentage composition of a gas mixture that contains not more than two hydrocarbons of the same group, provided the formula of each constituent is known.

If a gas mixture were to contain several gases of one group, say Group I, the equations between the knowns and unknowns would be derived as follows:

Let $x, y, z, \dots$ = volumes of the gases present
and $n, n', n'' \dots$ = indices of gases $x, y, z \dots$

Then (from Table I),

$$V = x + y + z + \dots \quad (5)$$

$$O_2 = \frac{3n+1}{2}x + \frac{3n'+1}{2}y + \frac{3n''+1}{2}z + \dots \quad (6)$$

$$CO_2 = nx + n'y + n''z + \dots \quad (7)$$

$$T.C. = \frac{n+3}{2}x + \frac{n'+3}{2}y + \frac{n''+3}{2}z + \dots \quad (8)$$

These four equations are not independent as can be shown by the following eliminations:

$$2O_2 - V - 3CO_2 = 0 \quad (2 \times \text{Eqn. 6} - \text{Eqn. 5} - 3 \times \text{Eqn. 7}) \quad (9)$$

$$2T.C. - CO_2 - 3V = 0 \quad (2 \times \text{Eqn. 8} - \text{Eqn. 7} - 3 \times \text{Eqn. 5}) \quad (10)$$

Equations 9 and 10 represent the peculiar relations that exist between the four determinable factors when the gases belong to the same group, and this relation is such that the determination of any two of these factors enables one to compute the other two; hence there are in reality only two independent equations, and *not more than two* gases of this group could be

determined by a single combustion. Similar relations hold true for the other groups and the analogous equations are given in the following table:

TABLE II

GROUP	EQUATIONS	
$C_nH_{2n} + 2$	$V = \frac{2 \text{ T. C. } - CO_2}{3}$	$V = \frac{3 CO_2 - 2 O_2}{-1}$
C_nH_{2n}	$V = \frac{2 \text{ T. C. } - CO_2}{2}$	$V = \frac{3 CO_2 - 2 O_2}{0}$ or $3 CO_2 = 2 O_2$
$C_nH_{2n} - 2$	$V = 2 \text{ T. C. } - CO_2$	$V = 3 CO_2 - 2 O_2$
$C_nH_{2n} - 4$	$V = \frac{2 \text{ T. C. } - CO_2}{0}$ or $2 \text{ T. C. } = CO_2$	$V = \frac{3 CO_2 - 2 O_2}{2}$
$C_nH_{2n} - 6$	$V = \frac{2 \text{ T. C. } - CO_2}{-1}$	$V = \frac{3 CO_2 - 2 O_2}{3}$

It is apparent also that the formulas of the individual gases are necessary, since otherwise two new unknowns, n and n' , would be introduced and the number of unknowns would exceed the number of independent equations.

A gas mixture that rather frequently occurs in technical practice is one containing hydrogen, methane and ethane. These three gases are hydrocarbons of the same group under the classification that is here employed, and since they belong to the same group, they cannot be determined by a single combustion. *If, in the analysis of this gas mixture, the results of the combustion are computed for hydrogen and methane alone, the volume of methane will be too large by twice the volume of the ethane that is actually present, and the volume of hydrogen will be too small by a volume equal to that of the ethane that is present, entirely independent of the relative percentages of each.*

The following calculation will make this clear:

Let H_2 , CH_4 and C_2H_6 represent the volumes of hydrogen, methane, and ethane in a mixture of these three gases.

Then, giving the proper values to n , n' and n'' in equations 7 and 8,

$$\text{T. C.} = \frac{3}{2} \text{H}_2 + 2 \text{CH}_4 + \frac{5}{2} \text{C}_2\text{H}_6 \quad (11)$$

$$\text{and CO}_2 = \text{CH}_4 + 2 \text{C}_2\text{H}_6 \quad (12)$$

Now, let x and y represent the amounts of hydrogen and methane obtained when the computation is based upon these two gases.

$$\text{Then T. C.} = \frac{3}{2} x + 2 y \quad (13)$$

$$\text{And CO}_2 = y \quad (14)$$

$$\frac{3}{2} x + 2 y = \frac{3}{2} \text{H}_2 + 2 \text{CH}_4 + \frac{5}{2} \text{C}_2\text{H}_6 \quad (\text{Eqn. 11} - \text{Eqn. 13}) \quad (15)$$

$$y = \text{CH}_4 + 2 \text{C}_2\text{H}_6 \quad (\text{Eqn. 12} - \text{Eqn. 14}) \quad (16)$$

$$x = \text{H}_2 - \text{C}_2\text{H}_6 \left(\frac{2}{3} [\text{Eqn. 15} - 2x \text{Eqn. 16}] \right) \quad (17)$$

For example, if a gas mixture contains equal volumes of hydrogen, methane, and ethane, and the combustion data are computed for hydrogen and methane alone, the result would indicate that the gas mixture contains only methane (see Equations 16 and 17).

In the analysis of such gas mixtures as coal gas, producer gas, or water gas the residue after the removal of the absorbable constituents is frequently assumed to consist of hydrogen, methane and nitrogen, and a calculation of the combustion results is based upon this assumption. It is clear from what has been stated above that this assumption may lead to errors of considerable magnitude in the percentages of hydrogen and methane if ethane is present. The percentage of nitrogen, however, is not affected, since the sum of the percentages of

hydrogen and methane apparently present is equal to the sum of the percentages of hydrogen, methane and ethane actually present.

SECOND CASE. It is possible, by means of one complete combustion, to determine the percentage composition of a gas mixture that contains not more than three hydrocarbons, two of them of the same group, provided the formula of each constituent is known.

If a gas mixture of this type were to contain two gases of Group I and one gas of each of the remaining groups, the equations would be derived as follows:

Let $x, y, z, \dots$ = volumes of the two gases of Group I and the gases from the other groups respectively, and $n, n', n'', \dots$ = indices of gases x, y, z , etc.

Then,

$$V = x + y + z + \dots \quad (18)$$

$$O_2 = \frac{3n+1}{2}x + \frac{3n'+1}{2}y + \frac{3n''}{2}z + \dots \quad (19)$$

$$CO_2 = nx + n'y + n''z + \dots \quad (20)$$

$$T. C. = \frac{n+3}{2}x + \frac{n'+3}{2}y + \frac{n''+2}{2}z + \dots \quad (21)$$

But inasmuch as

$$V + O_2 = CO_2 + T. C. \text{ (see Equation 1) } \dots \quad (22)$$

holds true for the combustion of any mixture of hydrocarbons, it is clear that if three of the four factors, V, O_2, CO_2 , and $T. C.$, are known, the fourth may be computed. From this it follows that there are really only three independent equations, and for this reason more than three hydrocarbons, two of them of the same group, cannot be determined by a single combustion. Moreover, as was shown under First Case, the formula of each gas must be known.

THIRD CASE. It is usually possible by means of one complete combustion to determine the percentage composition of a gas mixture that contains not more than three hydrocarbons, all of them of different groups, provided the formula of each constituent is known.

If a gas mixture of this type were to contain one gas from each group, the equations would be derived as follows:

Let $x, y, z, \dots$ = volumes of gases of 1st, 2d, 3d $\dots$ groups

And $n, n', n'' \dots$ = indices of gases, $x, y, z \dots$ etc.

Then

$$V = x + y + z + \dots \quad (23)$$

$$O_2 = \frac{3n+1}{2}x + \frac{3n'}{2}y + \frac{3n''-1}{2}z + \dots \quad (24)$$

$$CO_2 = nx + n'y + n''z + \dots \quad (25)$$

$$T.C. = \frac{n+3}{2}x + \frac{n'+2}{2}y + \frac{n''+1}{2}z + \dots \quad (26)$$

For the same reasons as those given under Second Case, *not more than three* hydrocarbons belonging to different groups can be determined, and the formula of each must be known. But in mixtures that would be classed under the Third Case there may exist a peculiar relation between the indices of the various gases that will render the equations indeterminate. For example, if a gas mixture contains one gas from each of the following groups, C_nH_{2n+2} , C_nH_{2n-4} , and C_nH_{2n-6} , then

$$V = x + y + z \quad (27)$$

$$2 O_2 = (3n+1)x + (3n'-2)y + (3n''-3)z \quad (28)$$

$$2 T.C. = (n+3)x + n'y + (n''-1)z \quad (29)$$

$$CO_2 = nx + n'y + n''z \quad (30)$$

Solving for x (or y or z),

$$(4n' - 3n'' - n)x = \text{some expression in terms of } V, O_2, T.C., \text{ and } CO_2. \quad (31)$$

When the relation between n , n' and n'' is such that

$$4n' - 3n'' - n = 0, \text{ or } n' = \frac{3n'' + n}{4}, \text{ the equation is inde-}$$

terminate. This is true when $n = n' = n'' = 1$, as for example when the gas mixture contains methane, carbon monoxide, and carbon dioxide.

Since the gases classified under the Third Case may belong to any one of five groups (see p. 129) there are ten possible combinations under this case.

If the five groups are represented by A, B, C, D, E, and the indices of the three gases in the mixture are represented by n , n' and n'' in the order of the groups, then the determinants and the indeterminate examples among the gases in Table I may be tabulated as follows:

TABLE III

COMBINATION	DETERMINANT	INDETERMINATE EXAMPLES
$\left. \begin{array}{l} \text{A B C} \\ \text{B C D} \\ \text{C D E} \end{array} \right\}$ A C E	$\left. \begin{array}{l} . \\ n' = \frac{n'' + n}{2} \\ . \end{array} \right\}$	$\left. \begin{array}{l} \text{C}_2\text{H}_6, \text{C}_2\text{H}_4, \text{C}_2\text{H}_2 \\ \text{C}_3\text{H}_8, \text{C}_2\text{H}_2, \text{CO}_2 \end{array} \right\}$
$\left. \begin{array}{l} \text{A B D} \\ \text{B C E} \end{array} \right\}$	$n' = \frac{n'' + 2n}{3}$	$\text{C}_3\text{H}_8, \text{C}_2\text{H}_4, \text{O}_2$
$\left. \begin{array}{l} \text{A C D} \\ \text{B D E} \end{array} \right\}$	$n' = \frac{2n'' + n}{3}$	
A B E	$n' = \frac{n'' + 3n}{4}$	
A D E	$n' = \frac{3n'' + n}{4}$	$\text{CH}_4, \text{CO}, \text{CO}_2$

FOURTH CASE. When a gas mixture contains hydrocarbons that belong to not more than two groups, the percentage of each group in the mixture may be determined by means of one complete combustion if the general formula of each group is known.

Let V be a mixture of two groups, of volumes X and Y to be determined, each a mixture of several gases $x_1, x_2, x_3, \dots$ and $y_1, y_2, y_3, \dots$.

Also let $n_1, n_2, n_3, \dots$ and $n'_1, n'_2, n'_3, \dots$ be the indices of the gases, and k and k' the constants of the two groups.

$$\text{Then } V = x_1 + x_2 + x_3 \dots + y_1 + y_2 + y_3 \dots \quad (32)$$

$$\text{CO}_2 = n_1 x_1 + n_2 x_2 + n_3 x_3 \dots + n'_1 y_1 + n'_2 y_2 + n'_3 y_3 \dots \quad (33)$$

$$\begin{aligned} 2 \text{ T. C.} &= (n_1 + k + 2) x_1 + (n_2 + k + 2) x_2 \dots \\ &+ (n'_1 + k' + 2) y_1 + (n'_2 + k' + 2) y_2 \dots \end{aligned} \quad (34)$$

$$\begin{aligned} 2 \text{ O}_2 &= (3n_1 + k) x_1 + (3n_2 + k) x_2 \dots + (3n'_1 + k') y_1 \\ &+ (3n'_2 + k') y_2 \dots \end{aligned} \quad (35)$$

$$\begin{aligned} 2 \text{ T. C.} - 2 V - 2 \text{ CO}_2 &= k(x_1 + x_2 + x_3 \dots) + k'(y_1 \\ &+ y_2 + y_3 \dots) \dots \end{aligned} \quad (36)$$

(Eqn. 34 — 2 Eqn. 32 — Eqn. 33)

$$2 \text{ T. C.} - 2 V - \text{CO}_2 = kX + k'Y \text{ (Simplifying Eqn. 36)} \quad (37)$$

$$V = X + Y \text{ (Simplifying Eqn. 32)} \dots \quad (38)$$

From equations 37 and 38 the values of X and Y can be determined when k and k' are known.

Gaseous Hydrocarbons and Nitrogen

If nitrogen is present with the gaseous hydrocarbons, the total contraction on combustion (see p. 128) is equal to the sum of the volume of the mixture and the volume of the necessary

oxygen, less the sum of the volume of carbon dioxide formed and the volume of nitrogen present, or

$$T. C. = V + O_2 - CO_2 - N_2 \quad . \quad . \quad . \quad . \quad (39)$$

where N_2 represents the volume of nitrogen in the gas mixture. The introduction of the unknown, N_2 , in the preceding equation renders the four equations between the four determinable factors and the unknowns independent when the hydrocarbons are not all of the same group (Second and Third Cases) and gives three independent equations when the hydrocarbons are all of the same group (First Case). Thus it is seen that the presence of nitrogen in a mixture that is otherwise composed entirely of hydrocarbons increases the number of independent equations by one and thereby provides for its own determination. In general, the determinability of any hydrocarbon mixture is not affected by the presence of an unknown amount of nitrogen.

This also holds true if the nitrogen be replaced by ammonia, or nitrous oxide, or hydrogen cyanide, if the necessary changes are made in the expressions involving O_2 , CO_2 , and $T. C.$

Summary

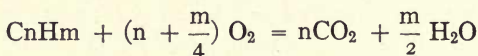
1. More than *three* gaseous hydrocarbons cannot be determined by one complete combustion.
2. Two gaseous hydrocarbons of known composition and of the same group can always be determined by one complete combustion.
3. Three gaseous hydrocarbons of known composition, two of which belong to the same group, can always be determined by one complete combustion.
4. Three gaseous hydrocarbons of known composition, but which belong to different groups, can usually be determined by one complete combustion (note exceptions).
5. In a mixture of hydrocarbons of two groups, the percent-

age of each group can be determined by one complete combustion.

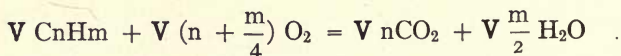
6. Any of the mixtures that have been mentioned above is still determinable even if an unknown quantity of nitrogen is present.

IDENTIFICATION OF GASEOUS HYDROCARBONS

To identify a gaseous hydrocarbon or to determine the relative amounts of carbon and hydrogen in a mixture of hydrocarbons, it is necessary only to burn a measured volume of the gas with oxygen and to determine the total contraction and the carbon dioxide formed. From these data the calculation may be made as follows:



and if V = the volume of the gas sample



Since the total contraction, $\text{T. C.} = V + \text{O}_2 - \text{CO}_2$ (see p. 128) then, in the present case,

$$\text{T. C.} = V + Vn + \frac{Vm}{4} - Vn \quad \text{or}$$

$$\text{T. C.} = V + \frac{Vm}{4} \quad \text{and}$$

$$m = \frac{4(\text{T. C.} - V)}{V}$$

$$\text{Since } \text{CO}_2 = Vn$$

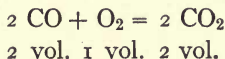
$$n = \frac{\text{CO}_2}{V}$$

In the determination of inflammable gases by combustion over mercury, it should be borne in mind that, if great accuracy is desired, correction must be introduced for the varia-

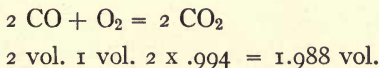
tion of the actual molecular volumes of certain gases from the molecular volumes calculated for these gases on the basis of Avogadro's hypothesis. The gram-molecular volume of a gas, that is, the volume, under standard conditions, occupied by the molecular weight of a gas in grams, is nearly the same in all cases, namely 22.4 liters. Yet the gases with which we chiefly have to do in combustion analysis show slight variations from this mean, and in one case, that of carbon dioxide, the difference is considerable.

	M	D _{H₂O} = 1	$\frac{M}{D}$	Mol.-Vol. Oxygen = 1
H ₂	2.016	0.00008988	22.43	1.0017
O ₂	32.00	0.0014291	22.39	1.0000
CO	28.003	0.0012507	22.39	1.0000
CH ₄	16.035	0.0071464	22.44	1.0020
CO ₂	44.003	0.001977	22.26	0.99393

In the gas volumetric comparison of hydrogen, oxygen, carbon monoxide and methane, the variations from one another do not amount to more than 0.2 per cent as will be seen from the figures in the last column of the table, where the molecular volumes are calculated on the basis of that of oxygen as unity. But, as Wohl has pointed out,¹ when gases that contain carbon are burned, an error too great to be disregarded in exact work will result if correction is not introduced for the low molecular volume of carbon dioxide. The molecular volume of CO₂ is 99.4 per cent that of CO. Consequently when CO is burned, the gas volume changes are accurately represented not by the usual equation



but by the following:



¹ *Ber. d. deutsch. chem. Ges.*, 37 (1904), 429.

If then the CO is calculated directly from the contraction, the result will be 1.2 per cent of the true volume of CO too high. Similarly if the CO is determined by absorption of the CO₂ formed, the result will be 0.6 per cent of the true volume of CO too low. For further details and for the statement of the slight corrections to be introduced in the determination of H₂ and CH₄ by combustion, the reader is referred to the article by Wohl.¹

¹ *Loc. cit.*

CHAPTER XII

THE DETERMINATION OF GASES BY COMBUSTION

ANALYSIS BY EXPLOSION

The Explosion Pipette for Technical Gas Analysis (Fig. 69).

— This consists of the thick-walled explosion-bulb *A* and the level-bulb *B*, which are joined together by a piece of enamelled

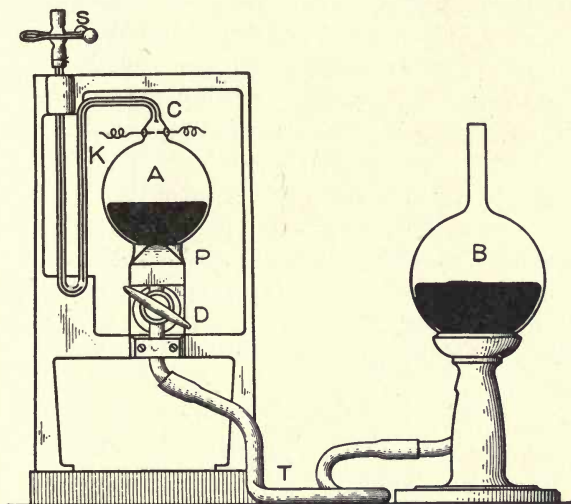


FIG. 69

rubber tubing *T*. The explosion bulb is supported by Plaster of Paris *P* as shown in the figure. At *C* two fine platinum wires are fused into the explosion pipette, the ends of the wires being about 2 mm. apart. At *D* is a glass stopcock, and the pipette terminates in the capillary *K*, whose end is closed by a short piece of rubber tubing *S* and a stout pinchcock.

The gas mixture that is to be exploded is introduced into the bulb *A*, the gas is brought approximately to atmospheric pressure, and the glass stopcock *D* is closed. The rubber tube *S* is next closed by the pinchcock, and a piece of glass rod is slipped into the end of the rubber tube. The pipette is then vigorously shaken to insure full mixture of the gases, the terminals at *C* are connected with the poles of an induction coil, a screen of plate glass is placed in front of the pipette and the current is turned on. The stopcock *D* is now opened at once, and the gas in the pipette is transferred without delay to the burette, and is measured at once if the burette is filled with mercury, or after one minute if the burette contains water.

In general, the pipettes and burettes for technical gas analysis are filled with aqueous solutions, but the explosion pipette is filled with mercury. By using mercury as confining liquid during the explosion it is possible afterward to determine the carbon dioxide formed in the combustion. If the explosion is made over water, a subsequent measuring of the carbon dioxide formed is inadmissible, because the pressure in the pipette is so high during the explosion that considerable quantities of carbon dioxide are absorbed by the water. By exploding over mercury very satisfactory results are obtained, even if the carbon dioxide is afterward measured in a burette that contains water as the confining liquid.

If the explosion is too violent it is possible that some oxides of nitrogen may be formed, if nitrogen is present. On the other hand, if the combustion in the pipette proceeds too slowly, the oxidation of the gases is probably not complete. The closing of the capillary of the explosion pipette in the manner above described furnishes not only a sort of safety-valve for the release of pressure if the explosion is too violent, but also affords means of judging the energy of the explosion. If the explosion has the proper intensity, there will be a quick jerk of the rubber tube at the moment of explosion, but both pinchcock and glass plug will remain in place. With too violent an explosion, the

pinchcock is forced open, and the glass plug is driven out of the rubber tube. If the combustion is not sufficiently vigorous, no movement of the rubber tube is seen. From these statements it is apparent that the suggestion to modify the Hempel explosion pipette by placing a glass stopcock at the upper end of the capillary *K*, not merely exposes the operator to the danger of accident through the bursting of the pipette, but also deprives him of a means of judging the intensity of the explosion.

Proportion of Gases in Analysis by Explosion. — Bunsen found that —

100 vol. of air with 13.45 oxyhydrogen gas would not burn.

					Vol. of Air remaining
100	air burned with	26.26	oxyhydrogen gas,	left	100.02
100	"	"	34.66	"	" 100.15
100	"	"	43.72	"	" 100.07
100	"	"	51.12	"	" 99.98
100	"	"	64.31	"	" 99.90
100	"	"	78.76	"	" 99.43
100	"	"	97.84	"	" 96.92
100	"	"	226.04	"	" 88.56

These results led Bunsen to recommend that in the determination of hydrogen by explosion not less than 26 volumes nor more than 64 volumes of combustible gas be used to 100 volumes of incombustible gas. It should, however, be borne in mind that the above proportions refer only to the explosion of mixtures of hydrogen and oxygen. With combustible gases other than hydrogen quite different ratios should be used. This is evidenced by the results of Teclu¹ who finds that mixtures of hydrogen, methane, acetylene and illuminating gas are explosive only when the amount of the combustible gas lies between the following percentage volumes: —

¹ *Jour. für praktische Chemie*, 75 (1907), 212. See also Burrell, *J. Ind. Eng. Chem.* 5 (1913), 181.

Hydrogen,	10	to	63	per cent
Methane,	3.5	"	7.9	"
Acetylene,	1.6	"	5.8	"
Illuminat- ing Gas	4.5	"	23.5	"

Formation of Oxides of Nitrogen. — It was long supposed that if the explosion of gas mixtures was made under the conditions that Bunsen laid down, the formation of oxides of nitrogen would always be avoided. Experimental evidence now seems to show that, when nitrogen is present, oxides of nitrogen are produced in varying amounts and that the quantity may at times be so appreciable as to introduce a considerable error in the results of analysis. A further source of possible error in the determination of hydrogen by explosion has been pointed out by Misteli¹ who states that small amounts of hydrogen escape combustion.

Induction Coil. — For producing the spark for the explosion an induction coil giving a spark about 15 mm. long will be found adequate. The current for operating this coil may be obtained from either dry or wet cells or from a storage battery or from a dynamo with sufficient resistance in the circuit.

The Hydrogen Pipette. — If a gas mixture contains so small an amount of combustible gas that it will not explode when mixed with oxygen or air, pure hydrogen or oxyhydrogen gas is added to the mixture. For the preparation of hydrogen gas for this purpose the hydrogen pipette (Fig. 70) may be used. This is a simple absorption pipette that has two small bulbs in the place of the first large bulb. Through the tube *g* a glass rod *h* is pushed up to the mouth of *e*. This rod is fastened tightly into *g* by means of a piece of rubber tube slipped over it, and it serves to hold pieces of chemically pure zinc in the bulb *e*. To fill the pipette it is inverted, the glass rod is taken out, and the pieces of zinc are dropped into *e*. The pipette is

¹ *Jour. für Gasbeleuchtung*, 48 (1905), 802.

then closed again, placed upright, and filled with dilute sulphuric acid (1:10) by means of a funnel. The pipette is closed at *i* with a piece of rubber tubing and a pinchcock.

After a short time the hydrogen produced will drive back the acid, so that the evolution ceases. Before drawing off the sample of hydrogen from the pipette it is advisable to drive out the gas in the pipette until the bulb *e* is completely filled with sulphuric acid. This may be done by blowing into a rubber tube attached to *c*. A new supply of pure hydrogen is now generated, and this gas may be used in the analysis. If several analyses are made one after another, this fresh evolution of the gas is unnecessary; but if the apparatus has stood for any length of time, air will diffuse through the sulphuric acid, and some oxygen and nitrogen will be found in the first portion of hydrogen that is drawn off. To obtain a more active evolution of hydrogen than that which takes place when pure zinc and pure acid are used, a few pieces of platinum foil may be put in with the zinc.

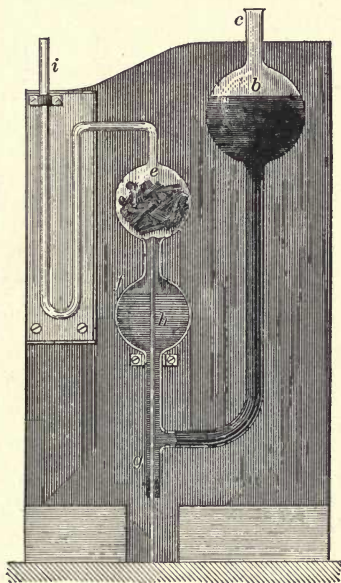


FIG. 70

Oxyhydrogen Gas Generator. — Oxyhydrogen gas may conveniently be generated in the apparatus of Hempel (Fig. 71), which is patterned after that described by Bunsen.¹ It consists of a glass cylinder into which there is inserted a cylindrical vessel *a* which is held in place by a cork fitting into the neck of the outer cylinder. The terminals *f* are platinum plates sus-

¹ *Gasometrische Methoden*, 2d ed. (1877), 77.

pendent on platinum wires that are fused into the sides of *a* and pass upward to the two mercury cups *d* and *e*. The outer cylinder is filled with water and the inner cylinder with dilute sulphuric acid (1:10). Into the neck of the inner cylinder *a* there is ground a glass tube that carries the bulb *c* and terminates in the bent capillary tube *b*. In the generation of oxyhydrogen gas by the electrolysis of acidulated water some

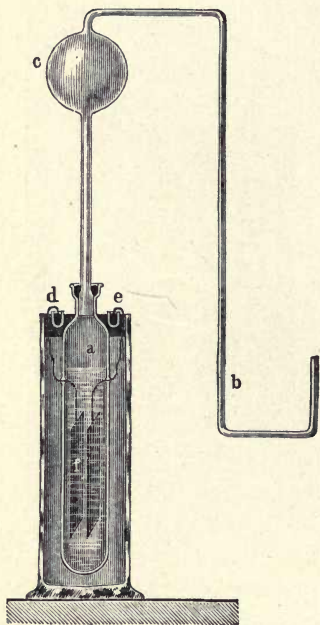


FIG. 71

ozone is always formed and this gas on being brought into the explosion pipette would unite with the mercury. This would cause a small excess of hydrogen in the oxyhydrogen gas. The ozone that is formed during the electrolysis may be converted into oxygen by exposing the oxyhydrogen gas, before using it, to the action of diffused daylight for twelve hours. It is to hasten this change that the bulb *c* of about 50 cc. capacity is placed between the generator and the capillary tube *b*. To prepare a sample of oxyhydrogen gas for use in explosion analysis, *d* and *e* are connected with a suitable source of current and oxyhydrogen gas is rapidly generated for about $1\frac{1}{2}$ hours. A little mercury is then introduced into the open end of

b and the generator is allowed to stand in the light for twelve hours.

The Explosion Pipette for the Hempel Apparatus for Exact Analysis (Fig. 72). — In the exact analysis also it is most convenient to make the explosions in a pipette specially constructed for the purpose. This pipette differs from the ordinary

pipettes only in having a stopcock at *a* and two platinum wires fused in at *b*.

To burn a gas mixture in this apparatus, the gas is brought into it in the usual manner, the stopcock is closed, and a fine sewing needle is placed in the mouth of the capillary *c*. Upon connecting the platinum wires with an induction apparatus, the mixture is exploded by the spark which passes when the circuit is closed.

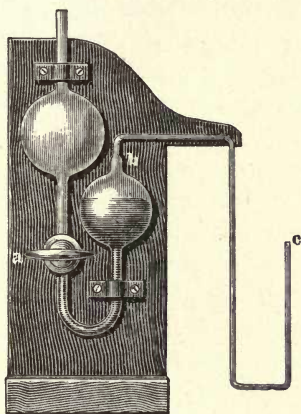


FIG. 72

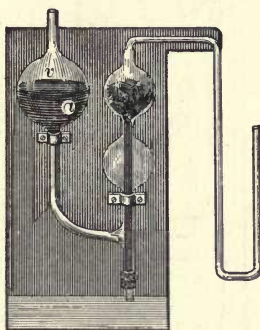


FIG. 73

Hydrogen for use in explosions in the Hempel exact analysis may be made in the pipette shown in Fig. 73.

The construction of this pipette resembles that of the hydrogen pipette shown and described on page 145.

ANALYSIS BY COMBUSTION

Combustion with an Electrically Heated Platinum Spiral

The Combustion Pipette. — Coquillion was the first to propose the use of the glowing platinum spiral in the determination of such gases as marsh-gas and hydrogen. Winkler improved the form of the apparatus and used a Hempel pipette for solid

and liquid reagents. While adhering in the main to the Winkler arrangement, the author has modified the apparatus so that mercury may be used as the confining liquid. This permits of a much more accurate determination of carbon monoxide or hydrocarbons than is possible over water. The cylindrical portion of a Hempel simple pipette for solid and liquid reagents, *A*, Fig. 74, is fastened to the stand in the usual manner, except that the bulb is supported by a small

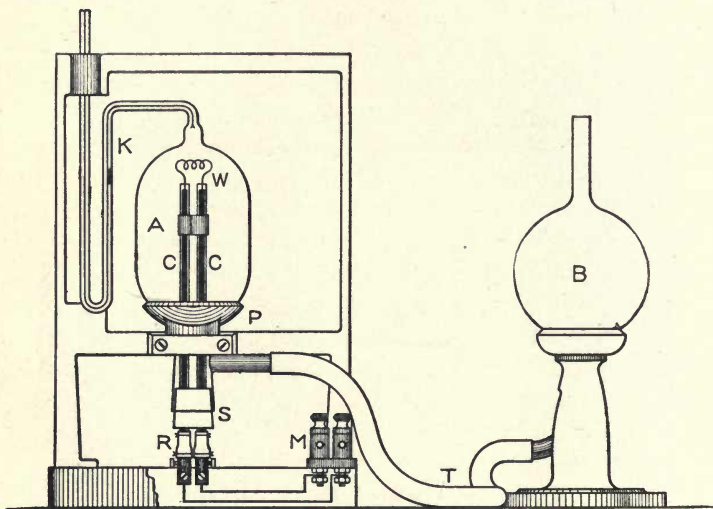


FIG. 74

block of Plaster of Paris, *P*. In the neck of the pipette is inserted a two-hole rubber stopper *S* through the openings of which glass tubes *cc* pass from below the stopper to within about 20 mm. of the top of the pipette. Inside of each glass tube is a stout iron wire 2.5 mm. in diameter which reaches nearly to the top of the glass tube and projects about 10 mm. below the lower end. To the lower end of each iron wire there is attached a small binding post and the connection between the glass tube and the binding post is made air-tight by slipping over the

ends of each a short piece of rubber tubing *R* which is then securely wired in place. Small iron screws are threaded into openings in the upper ends of the two iron wires, and serve to hold in place the ends of the platinum spiral *W*. A strip of iron about one cm. wide is bent in the form of an S around the two glass tubes about midway up in the bulb of the pipette for the purpose of holding the tubes more rigidly in position. The platinum spiral that connects the upper ends of the two iron wires is made of platinum wire $\frac{1}{4}$ mm. in diameter which is bent in a coil about 2 mm. in diameter and contains from 20 to 30 turns. The ends of the platinum wire are fastened under the two small screws in the upper ends of the iron wires. The two binding posts that are fastened to the lower ends of the iron wires are connected to two larger binding posts *M* fastened into a plate of hard rubber that is itself attached to the base of the iron frame. The combustion pipette is usually filled with mercury which is introduced through a small funnel inserted in the tube of the level-bulb *B*. After the pipette has been filled with the mercury, the air that may be trapped by the mercury in the glass tubes surrounding the iron wires is removed by closing the capillary tube of the pipette with a piece of rubber tube and pinchcock and attaching a water suction pump to the tube of the level-bulb.

When the pipette is constructed and is filled with mercury in the manner above described, the iron wires passing through the glass tubes do not come into contact with the gas mixture in the pipette at any point, for when a gas is passed into the pipette the glass tubes remain filled with mercury which covers the ends of the iron wires. This makes it entirely unnecessary to use heavy platinum wires in the place of the iron wires as has been recommended by Porter and Ovitz.¹

Manipulation of the Combustion Pipette. — In carrying out a combustion with this pipette a measured amount of oxygen (about 100 cc.) is passed into it from a gas burette and the gas

¹ *Bulletin 1, Department of the Interior, Bureau of Mines, 1910, p. 24.*

to be burned is then measured off in the burette. Ordinarily the total unabsorbable residue from a gas sample of about 100 cc. is used in the combustion, but the volume of the sample taken should be of such size that after combustion an excess of oxygen remains in the pipette. The gas burette *H* is connected with the combustion pipette by the usual bent capillary tube, and the wires from the source of current are fastened to the binding posts on the frame of the pipette, Fig. 75. A small rheostat *R* is introduced into the circuit to permit of ready control of the current flowing through the platinum spiral and thus to enable the operator to keep the spiral at dull redness throughout the combustion. The current for heating the spiral may be that from a storage battery or from a dynamo, or more conveniently the alternating current of a lighting circuit. If the alternating current is employed, the connections may be made as shown in the figure. A plug carrying two wires is screwed into an ordinary lamp socket; one of the wires is connected with the rheostat and the other with a bank of lamps *L* connected in parallel. The further terminal of the lamps is connected with one of the binding posts *M* on the pipette, and the other binding post is connected with the rheostat *R*. The coarser adjustment of the current is made by means of the lamps and the finer adjustment by means of the rheostat.

Different gases show great differences in heat conductivity and if adjustment of the current were not easily possible the spiral might be raised to so high a temperature during the process as to melt the platinum wire. For example, when hydrogen is burned in the pipette by first introducing that gas and then admitting a mixture of air and oxygen, a current that will at the beginning heat the spiral only to redness in the atmosphere of hydrogen will bring the platinum wire to a bright yellow glow and will at times melt it in the mixture of nitrogen and oxygen that remains after the hydrogen has been burned. After the combustible gas has been introduced, the platinum spiral is kept at dull redness for 60 seconds. The current is then

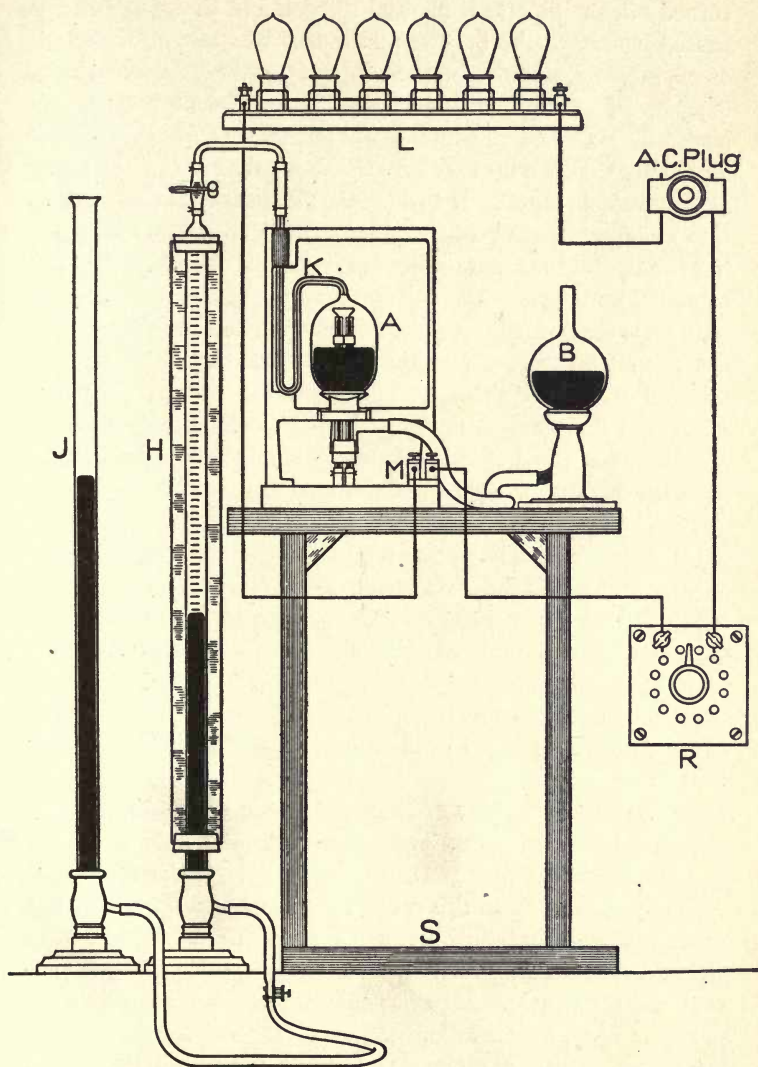


FIG. 75

turned off, the pipette is allowed to cool, and the gas residue is passed back into the burette and measured. Air or a mixture of oxygen and air may be used in the pipette in place of pure oxygen. If the combustible gas contains acetylene or its homologues it should be run into the pipette very slowly and under a pressure that is only very slightly above that of the prevailing atmospheric pressure. If this precaution is not taken, dissociation is liable to occur when the gas comes in contact with the hot spiral, and the separated carbon would of course then escape combustion.

In most cases the process may be reversed and the combustible gas be first introduced into the pipette, and oxygen or air or a mixture of the two then passed in from the burette. This manipulation is, however, not suited to the combustion of acetylene because the hot spiral causes decomposition of this gas with the deposition of solid carbon.

The chief merits of this method of combustion are:

- (1) The use of a large volume of combustible gas with consequent increase in the accuracy of the results;
- (2) The avoidance of explosion by the *gradual* addition of oxygen to the combustible gas or of the combustible gas to oxygen;
- (3) The avoidance of the formation of measurable amounts of the oxides of nitrogen in the combustion of gas mixtures that contain nitrogen.

Formation of Oxides of Nitrogen in Combustion Pipette.

— A. H. White has described experiments¹ that lead him to state that oxides of nitrogen are formed when hydrogen is burned with oxygen and air in this pipette, and he bases this statement upon the fact that he obtained a reaction for nitrites with Griess's reagent after heating air alone in the combustion pipette, and further that there was contraction in volume when the products of the combustion of hydrogen with oxygen and air were passed into a pipette containing potassium hydroxide.

¹ *Jour. Am. Chem. Soc.*, 23 (1901), 476.

F. H. Rhodes has, at the request of the author, carefully repeated and extended the experiments of White, and he finds that no measurable amount of oxides of nitrogen is formed when the conditions that were given in the original article of Dennis and Hopkins¹ are followed, and the platinum spiral is heated only to dull redness during the combustion and is kept at dull redness for no longer than sixty seconds after the gases have been introduced into the pipette. Upon passing air that has been heated in this manner in the pipette through 5 cc. of an 8% solution of pure sodium hydroxide, acidifying this with acetic acid and adding 1 cc. of Griess's reagent, there resulted a color which, on comparison with a nitrite solution of known strength, showed that not more than a trace of oxides of nitrogen was produced under these conditions. When the spiral was heated for *five minutes* to a temperature of dull redness in 100 cc. of air, the colorimetric determination of the nitrite that was formed showed that the amount of the oxides of nitrogen produced did not in any case exceed $\frac{1}{200}$ of a cc., and that the volume is usually much less than this. When the temperature of the spiral was raised beyond a dull red heat, the amount of the oxides of nitrogen that was formed increased with rise of temperature, but the total amount of the product even after heating the air for five minutes with the spiral at a bright yellow was not measurable in a Hempel burette over mercury.

In the combustion of hydrogen with a mixture of oxygen and air, Rhodes found that when the spiral is properly heated, the amount of oxides of nitrogen that was produced is slightly higher than when air alone is heated, but that the volume of this product was in no case large enough to permit of its volumetric measurement when 100 cc. of hydrogen was burned. To ascertain whether an appreciable error would result in the combustion of hydrogen with a mixture of air and oxygen when the spiral was highly heated, 100 cc. of hydrogen was introduced into the pipette, the spiral was heated to bright yellow, and

¹ *Jour. Am. Chem. Soc.*, 21 (1899), 398.

100 cc. of a mixture of equal volumes of air and oxygen was slowly passed in. The colorimetric determination of the amount of nitrite formed when the products were passed into the sodium hydroxide showed that even under these unusual conditions, the volume of the oxides of nitrogen that was formed was less than $\frac{1}{100}$ of a cc., an error that is entirely negligible in technical gas analysis when working with a gas sample of 100 cc. In the analysis of gas mixtures that commonly occur in technical practice, the error would be very much less than that above cited because of the lower percentage of hydrogen. As a further check upon the above results a mixture of 1 cc. of nitrogen tetroxide and 99 cc. of air was made in a Hempel burette over mercury. 99 cc. of this mixture was then driven out of the burette and the residual 1 cc. of gas was diluted with a further 99 cc. of air. This total gas volume, now containing 0.01 per cent of nitrogen tetroxide, was passed through a solution of sodium hydroxide. The solution was acidified with acetic acid and Griess's reagent was then added. The depth of color of this solution was found to be much greater than that resulting from a similar treatment of the gases produced by the different methods of combustion described above, and this held true even when the hydrogen was burned under conditions most favorable to the formation of oxides of nitrogen, namely, high temperature of the spiral and slow introduction of the gas.

Combustion with a Platinum Capillary Tube (Drehschmidt)

The determination of combustible gases by explosion or by combustion in the combustion pipette necessitates the employment of an electric current. With the apparatus devised by Drehschmidt¹ the combustible gases mixed either with air or with pure oxygen may be burned without danger of explosion in a platinum capillary tube that is heated to the requisite temperature by means of a gas flame. In the original form

¹ *Berichte d. deutsch. chem. Ges.*, 21 (1888), 3242.

proposed by Drehschmidt the platinum combustion tube was given a length of 200 mm. to prevent the ends of the tube from becoming too warm. Winkler improved the device by fitting a water jacket to each end of the tube which rendered it possible to reduce the platinum tube to a length of 100 mm. The Winkler form of tube is shown in Fig. 76. The combustion tube *P* is of platinum and has a length of 100 mm., an external diameter

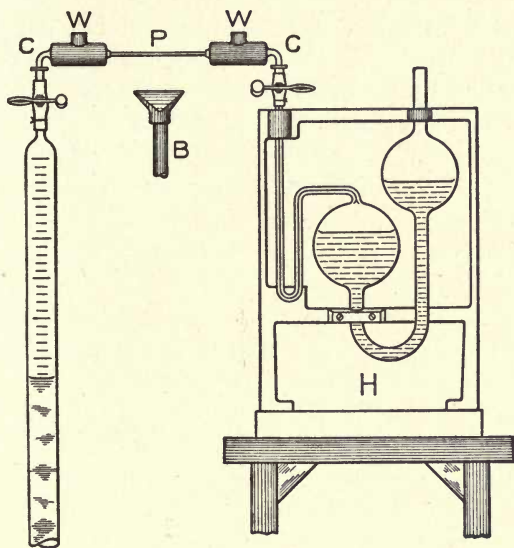


FIG. 76

of 2.5 to 3 mm. and an internal diameter of 0.7 mm. The tube should not be lap-welded but should be bored or drawn. Inasmuch as an explosive gas mixture is passed through the tube from the gas burette, it is necessary to prevent the propagation of the combustion from the tube to the gas mixture in the burette. This is accomplished by filling the platinum tube with fine platinum wires. The ends of the combustion tube are soldered to copper tubes *CC* that have an external diameter

of about 3.5 mm. and an internal diameter of 1.5 mm. These tubes are bent at right angles as shown in the figure and their horizontal portions are also filled with fine platinum wires. The water jackets, *WW*, are of sheet brass and are about 5 cm. long and 2.5 cm. wide. They are fastened upon the tube in such position that the junctions of the platinum and copper lie within the water coolers. Each jacket has an opening in the top for the introduction of cold water.

Before being put in use the combustion tube should be carefully tested to ascertain whether it is tight. This may be done by connecting a glass tube about 20 cm. long to one of the copper tubes, immersing the lower end of the glass tube in mercury, joining the other copper tube to a water suction pump by means of a piece of rubber tubing and drawing up the mercury in the glass tube to a height of about 10 cm. The rubber tube is then closed by a pinchcock. If the tube does not leak the mercury in the glass tube will not fall. If the tube is found to be tight at ordinary temperatures, the pinchcock is opened, the platinum tube is heated by a Bunsen flame and the test is then repeated. In the experience of the author the chief objection to the Drehschmidt tubes that are now on the market lies in the fact that they begin to leak after having been in use only a comparatively short time. This constitutes a serious drawback when the high cost of the tube and the difficulty of repairing it in the laboratory are taken into consideration.

In carrying out a combustion with this apparatus the measured sample of gas to be burned is passed over into the simple gas pipette *H*, and an amount of air or oxygen that is surely sufficient to burn the combustible constituents of the gas mixture is measured off in the gas burette. This is then passed into the pipette and the pinchcock at the top of the pipette is closed. The Drehschmidt tube is then placed in position as shown in the figure, the burette being of course filled to the top with the confining liquid. The platinum combustion tube *P* is heated to bright redness by means of the burner *B*, the pinchcocks on

the pipette and burette are then opened and the gas is slowly drawn over into the burette. Two passages of the gas through the capillary suffice for complete combustion. The platinum tube is then allowed to cool and the residual gas is drawn into the burette and measured. The simple pipette is now replaced by a pipette containing potassium hydroxide, and the carbon dioxide is removed and the gas residue is again measured. If hydrogen and methane are being simultaneously determined, results of only approximate accuracy are obtainable when water is used as the confining liquid in the burette and pipette. In such case it is therefore preferable to use a pipette with level-bulb (see Fig. 51) and to employ mercury as the confining liquid in both the pipette and the burette.

CHAPTER XIII

PROPERTIES OF THE VARIOUS GASES AND METHODS FOR THEIR DETERMINATION

OXYGEN

Properties of Oxygen. — Specific gravity, 1.1055¹; weight of one liter, 1.4292 gram; critical temperature, — 118°; critical pressure, 50 atmospheres.

Oxygen is but slightly soluble in water. One liter of water absorbs, from atmospheric air, according to L. W. Winkler,² Otto Pettersson, and K. Sonden,³ at 760 mm. pressure: —

at 0° C.	10.01	cc.
" 6° C.	8.3	"
" 9.18° C.	7.9	"
" 14.1° C.	7.05	"
" 16.87° C.	6.84	"
" 23.64° C.	5.99	"
" 24.24° C.	5.916	"

and of pure oxygen, according to Bunsen —

at 20° C., 28.38 cc.

One volume of alcohol absorbs, according to Carius, at all temperatures between 0° and 24°, 0.28397 volume.

Determination of Oxygen. — Oxygen may be determined either by mixing it with an excess of hydrogen and exploding

¹ Most of these figures are from Landolt and Börnstein's *Physikalisch-chemische Tabellen*.

² *Berichte der deutschen chemischen Gesellschaft*, 21 (1888), 2843.

³ *Ibid.*, 22 (1889), 1443.

the mixture, or by passing the gas into a combustion pipette containing an excess of hydrogen, or by bringing it into contact with glowing metallic copper, or by absorption of the gas.

Determination of Oxygen by Combustion. — The explosion analysis may be carried out in the apparatus described on page 141.

The combustion may most conveniently be performed in the pipette shown in Fig. 74.

In either of these methods two volumes of hydrogen unite with one volume of oxygen to form liquid water. The volume of oxygen present is consequently equal to $\frac{1}{3}$ of the contraction of the gas volume.

The hydrogen needed for these analyses may be prepared in the hydrogen pipette (Fig. 70) or it may be generated by the electrolysis of water in the Bunsen apparatus,¹ in which the positive pole consists of a zinc wire floating in mercury. In the determination of oxygen by explosion with hydrogen, the oxygen should be mixed with from three to ten times its volume of hydrogen. If the amount of oxygen in the original gas mixture is quite low, there should be added, in addition to the hydrogen, an amount of oxyhydrogen gas sufficient to render the mixture explosive.

Determination of Oxygen with Copper Eudiometer. — Very accurate determinations of oxygen may be made by combustion with copper. U. G. Kreusler has so improved the apparatus devised by Ph. v. Jolly for the determination of oxygen in the atmosphere that it is now one of the most exact methods known. A so-called copper eudiometer, whose construction is based upon his well-known air thermometer, is used for the determination. The air whose oxygen contents is to be determined is admitted into a bulb that has previously been completely exhausted, and the pressure is read off on a very exact mercury manometer. The oxygen is then absorbed by a copper spiral that is heated to glowing by a strong electric current;

¹ *Gasometrische Methoden*, 2d ed. (1877), p. 80.

the metallic copper is changed to cuprous and cupric oxide. After the apparatus has become cool, the remaining nitrogen is brought to the initial volume by changing the pressure, and a reading is taken of the pressure now prevailing.¹ When due regard is given to all the necessary precautions, the method is of the greatest exactness; it is, however, very complex and tedious, and for this reason is not well suited to the making of a large number of determinations.

Determination of Oxygen by Absorption. — Oxygen may rapidly and accurately be determined by means of various absorbents, among the best of which are —

1. A strongly alkaline solution of pyrogallol,
2. Phosphorus in solid form,
3. Phosphorus in solution,
4. Metallic copper,
5. Solutions of ferrous salts,
6. Sodium hyposulphite,
7. Chromous chloride.

1. *Alkaline Pyrogallol*

Hempel prepares the alkaline solution of pyrogallol by dissolving 120 grams of potassium hydroxide not purified by alcohol in 80 cc. of water and adding to this 5 grams of pyrogallol dissolved in 15 cc. of water. The two solutions are brought together in a double absorption pipette (Fig. 36) or in the apparatus described on page 161. Hempel states that a solution prepared as above gives off no carbon monoxide during the absorption, or at most only such slight amounts that the error thus caused falls within the limit of the error of the readings. Benedict,² however, appears to be of the opinion that the reagent thus prepared will set free some carbon monoxide although

¹ U. Kreusler, *Ueber den Sauerstoffgehalt der atmosphärischen Luft*. *Landwirthschaftliche Jahrbücher*, 1885, p. 305.

² *The Composition of the Atmosphere*, Publication No. 166 of the Carnegie Institution of Washington, 1912, p. 113.

he gives no experimental proof that it does so. He recommends that the absorbent be prepared as follows: 500 grams of stick potassium hydroxide, not purified by alcohol, is dissolved in 250 cc. of water. The specific gravity of the solution is usually 1.55, but, if it varies materially from this figure, more potassium hydroxide or more water is added until the density of 1.55 is reached. 135 cc. of this solution is added to a solution of 15 grams of pyrogallol in 15 cc. of distilled water.

The determination should not be made at a temperature much below 15° , for the absorption by alkaline pyrogallol is very much less active at a temperature under 7° . At a temperature of 15° or higher, the last trace of oxygen can be removed with certainty in the space of three minutes by shaking with the solution of alkaline pyrogallol, while at lower temperatures the absorption is not complete after six minutes. The analytical absorbing power of the solution is from 2 to $2\frac{1}{4}$.

If a large number of oxygen determinations is to be made by the "exact" method, the reagent is kept in the apparatus shown in Fig. 77. With this device a large quantity of the reagent may be stored, measured off, and transferred to the absorption pipettes without coming in contact with the air.

The large reservoir bulb *A* ends above in the U-shaped tube *B*, which has a short side-arm at *f* and ends in the T-shaped capillary *g*. To the lower side of the bulb is attached the bent tube *h*, which is provided with a glass stopcock *i*. A small funnel can be fastened to the upper end of *h* by a rubber tube *k*. A thin rubber tube connects the side-arm *f* with the funnel *o*. The ends of the T capillary *g* are provided with short pieces of rubber tubing and with pinchcocks. The apparatus is first filled completely with mercury. A funnel or glass tube is then inserted in the free end of *m*, the pinchcocks *n* and *y* are closed, the stopcock *i* is opened, and the aqueous solution of pyrogallol is poured into the funnel attached to *m*. The end *k* of the tube *h* is now connected by a rubber tube with a suction flask, and the flask is joined to an aspirator. Upon opening the pinchcock

at *m* the mercury flows through *h* into the flask, and the solution of pyrogallol is drawn into *A*. The entrance of the reagent can instantly be stopped by turning the stopcock *i*. When all of the pyrogallol has entered the pipette, the solution of potas-

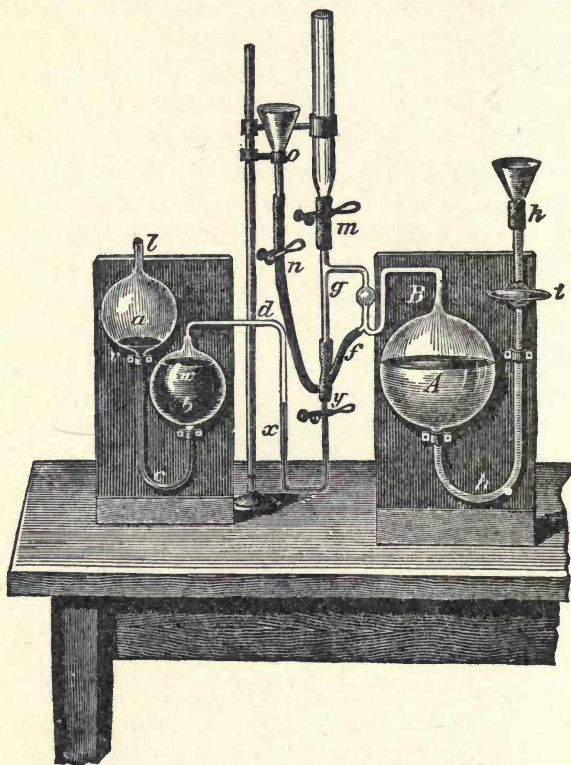


FIG. 77

sium hydroxide is poured into the funnel and drawn in in the same manner. The two solutions in the apparatus are then thoroughly mixed by shaking.

To transfer some of the reagent to a pipette, the apparatus is arranged as shown in Fig. 77. The capillary of the pipette

is inserted at *y* into the end of the rubber tube attached to the lower end of *g*. By blowing into *l* (this can best be done with the rubber pump, Fig. 8) the mercury in the pipette is driven to *g*, and *m*, *n*, and *y* are then closed. Some mercury is poured into the funnel inserted in *k*, and *i* is opened. Upon lowering the funnel *o* and opening the pinchcock *n*, the left side of the U-shaped tube *B* can easily be filled down to a mark with the reagent, for the mercury drives the reagent out of the bulb into *B*. When the reagent has thus been measured off, *i* is closed, *y* is opened, and by raising the funnel *o* the reagent is driven over into the pipette until the mercury reaches the point *x*. The pipette is then disconnected, the capillary *d* is immersed in a beaker of distilled water, and by careful alternate sucking and blowing at *l* the capillary is freed within and without from the last traces of the reagent. It is then dried with filter paper, and the pipette is ready for use.

2. *Solid Phosphorus*

The method of Lindemann for the absorption of oxygen by solid phosphorus gives, under proper conditions and in the absence of gases that inhibit the reaction, very accurate results. The amount of phosphorus contained in a Hempel gas pipette is capable of absorbing a very large volume of oxygen, in which respect it is superior to alkaline pyrogallol which has a relatively small absorbing power.

Phosphorus does not, however, unite with oxygen when the gas has a high partial pressure. If the oxygen is nearly pure, no reaction takes place between it and phosphorus, and only when its pressure is lowered either by dilution with another gas, or by partial exhaustion with an air-pump, does a union of the phosphorus and oxygen result. The reaction between the two elements is explosive in character when the gas mixture contains from 50 to 75 per cent of oxygen, but it proceeds quietly when less than 50 per cent of oxygen is present. It is unsafe

to use the method for the determination of oxygen in gas mixtures that contain enough hydrogen to render them explosive, because the rise of temperature caused by the interaction of the phosphorus and oxygen may ignite the mixture. In such case, or when the mixture contains over 50 per cent of oxygen, the gas should be absorbed by some agent other than phosphorus.

The union of phosphorus with oxygen is prevented or greatly retarded by the presence of even small amounts of certain other gases, such as ethylene, acetylene, some other hydrocarbons, some ethereal oils, alcohol or ammonia.

The reaction is further dependent upon the temperature. It proceeds normally at about 20° C., while at 14° it takes place quite slowly, so that a quarter of an hour or longer is required to completely separate the oxygen from 100 cc. of air. At 10° and still lower temperatures a half hour's time would not be sufficient. It follows from this that during the colder months of the year the absorption must be carried out in warm rooms.

The absorption of oxygen by phosphorus may conveniently be effected by passing the gas mixture into a Hempel simple pipette for solid and liquid reagents (Fig. 35) that contains sticks of phosphorus immersed in water.

Phosphorus may be purchased on the market in the form of thin sticks ready for use, or it may be prepared by the analyst himself in this form in the following manner:— A test tube is filled with water, and sticks of phosphorus of the ordinary commercial size are introduced into the tube. The tube is then placed in a metal water bath in which the temperature of the water is maintained at about 50° . The phosphorus readily melts and it is protected from the action of the air by the water above it. Enough phosphorus should be used to form in the test tube a column of molten phosphorus about 7 cm. high. A 2-liter beaker full of cold water is placed near the water bath. A glass tube with slight taper and about 3 mm. internal diameter

is then pushed down to the bottom of the test tube containing the molten phosphorus, the upper end of the tube is closed with the moistened finger, and the tube, carrying a column of the molten phosphorus with a little water above it, is quickly lifted out of the test tube and dipped into the beaker of cold water. If the walls of the glass tube are not too thick, the phosphorus soon solidifies and since it decreases in volume on changing from the liquid to the solid state the stick will usually fall out of the tube of itself. If it adheres to the walls it may easily be pushed out with a wire. The cylindrical part of the gas pipette in which the phosphorus is to be placed should be of brown glass to protect the phosphorus from the action of the light (see p. 56). If such pipettes are not available the whole pipette when not in use should be covered by a light-tight box of wood or cardboard. The pipette is filled by turning it upside down, removing the stopper of the cylindrical portion, filling the cylinder with water, and then introducing the small sticks of phosphorus until the cylinder is tightly packed with them. The stopper of the cylinder is then inserted and the pipette is turned into upright position.

In the absorption of oxygen the water in the pipette is first driven up in the capillary and to the end of the connecting bent capillary tube by blowing into a rubber tube attached to the wide tube of the end bulb. The connecting capillary tube is then inserted into the rubber tube of the burette and the gas mixture is passed over into the phosphorus pipette, the water or mercury from the burette being allowed to follow nearly to the cylinder of the pipette. The union of the phosphorus with the oxygen is complete in three minutes or less, the end of the reaction being shown by the disappearance of the glow when the pipette is in a dark room. Inasmuch as the different oxidation products of phosphorus are soluble in water, the surface of the sticks of phosphorus is freed from these substances by the solvent action of the confining water provided the water is renewed from time to time.

3. *Phosphorus in Solution*

Centnerszwer has suggested¹ the employment of a solution of phosphorus in oil as an absorbent for oxygen in gas analytic work. The reagent is prepared by placing about 230 cc. of castor oil in a 250 cc. flask, dropping into the oil three grams of well dried phosphorus, and after lightly closing the neck of the flask with a stopper, heating the contents in an oil bath to 200°. The hot flask is then removed from the bath, the stopper is tightly inserted, and the flask is wrapped in a towel and vigorously shaken until complete solution of phosphorus is effected. When cool the solution is ready for use. It is introduced into a Hempel double absorption pipette for liquid reagents by joining to the wide tube of the pipette, by means of a piece of rubber tubing, a wide glass tube bent downward, allowing this to dip into the oil and drawing the reagent into the further bulbs of the pipette by applying suction to the capillary tube of the pipette.

In absorbing oxygen, the gas mixture is passed over into the pipette in the usual manner and is allowed to stand in contact with the oil solution of phosphorus as long as a glow can be observed. No harm results if some water happens to pass from the burette into the pipette. After the glow in the pipette has disappeared, the remaining gas is drawn back into the burette and measured. Centnerszwer states that the reagent can be used for the determination of oxygen in gas mixtures that are high in oxygen, and the confirmatory analyses that he cites seem to show that the method is fairly accurate.

4. *Copper*

A very active absorbent for oxygen is metallic copper in the form of little rolls of wire-gauze, immersed in a solution of ammonia and ammonium carbonate.

¹ *Chemiker-Zeitung*, 34 (1910), 494.

It has long been known that many metals oxidize readily in the presence of vapor of ammonia. The absorption of oxygen, however, takes place rapidly only so long as the metallic surface is bright, and it proceeds very slowly as soon as considerable quantities of oxide are formed.

A very rapid and complete absorption of oxygen results when the gas is brought into contact with metallic copper and a solution consisting of equal parts of a saturated solution of commercial ammonium sesquicarbonate and a solution of ammonia of 0.93 specific gravity. Such an ammoniacal solution has a tension that may in most cases be disregarded, and, provided the absorption apparatus contains sufficient metallic copper, the solution can easily absorb 24 times its volume of oxygen. Its analytical absorbing power is therefore 6. Since the surface of metallic copper is frequently covered with a thin layer of grease, it is necessary to clean it before using by exposing it for a moment to the action of nitric acid.

The reagent is used in the same manner as solid phosphorus, in a pipette for solid absorbents. In making the absorption, the gas is allowed to remain in the pipette for five minutes.

The method described admits of a very rapid and exact determination of oxygen. As compared with alkaline pyrogallol, copper has a much greater absorbing power for oxygen, and it has the advantage over phosphorus, aside from the danger attending the use of the latter, of absorbing equally well at any temperature, while the absorption of oxygen by phosphorus takes place quite slowly at temperatures below 14° C. Direct experiments showed that at a temperature of -7° C. the absorption of oxygen in the air was complete in five minutes.

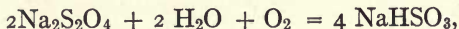
In the analysis of gas mixtures that contain carbon monoxide the method cannot be used, because the basic ammonium cuprous carbonate, formed from the copper present, absorbs carbon monoxide.

5. *Solutions of Ferrous Salts*

The oxygen in gas mixtures containing carbon monoxide can, according to Kostin, be removed by the use of a pipette filled with iron wire gauze that stands in a saturated solution of ferrous sulphate to which has been added one-third of its volume of strong ammonia. It is preferable to employ a solution of ferrous chloride to which has been added ammonia and sufficient ammonium chloride to prevent the separation of ferrous hydroxide.

6. *Sodium Hyposulphite*

Hyposulphurous acid was first prepared in 1868 by Schützenberger. The formula of the compound was correctly determined by Bernthsen¹ in 1880. The sodium salt of the acid has recently become easily obtainable and for that reason Franzen² has examined the substance with a view to ascertaining whether it could be used in gas analysis for the absorption of oxygen. He prepares the reagent by dissolving 50 grams of sodium hyposulphite in 250 cc. of water, and 30 grams of sodium hydroxide in 40 cc. of water, and mixing the two solutions. This final solution is placed in a Hempel pipette for solid reagents that has first been filled with small rolls of iron wire gauze. Franzen states that in this apparatus oxygen, if present in not too large amount, is completely absorbed in five minutes. The reaction that takes place is represented by the equation



from which it appears that one gram of sodium hyposulphite is able to absorb about 64 cc. of oxygen. One cc. of the above solution will consequently absorb 10.7 cc. of oxygen, and its analytical absorbing power (see p. 65) will therefore be about 2.5. Franzen enumerates the following advantages possessed

¹ *Berichte der deutschen chemischen Gesellschaft*, 13 (1880), 2277.

² *Berichte der deutschen chemischen Gesellschaft*, 39 (1906), 2069.

by sodium hyposulphite over other absorbents for oxygen. In the first place it is decidedly cheaper than pyrogallol; ¹ secondly, it absorbs oxygen as rapidly at low temperatures as it does at higher, whereas the absorbing power of alkaline pyrogallol and of phosphorus shows marked decrease with fall of temperature. Furthermore the absorption of oxygen by the reagent is not influenced by gases that prevent the oxidation of phosphorus.

If the reagent is to be used in the Bunte burette for the determination of oxygen Franzen recommends the use of a solution somewhat less concentrated than that described above, and employs for this purpose a solution of ten grams of sodium hyposulphite in 50 cc. of water to which has been added 50 cc. of a ten per cent solution of sodium hydroxide. Shaking for three minutes suffices to completely remove the oxygen when that gas is present in not too great amount.

7. Chromous Chloride

Chromous chloride may be used for absorbing oxygen ² in the presence of hydrogen sulphide and carbon dioxide. These two gases are completely indifferent to both the blue chromic chloride and the green chromous chloride solutions.

Dennstedt and Hassler, however, state ³ that as an absorbent for oxygen it is open to objection because it easily gives off hydrogen.

To prepare chromous chloride, Von der Pfordten has used the method given by Moissan. A green solution of chromic chloride free from chlorine is made by heating chromic acid with concentrated hydrochloric acid, and this solution is then reduced with zinc and hydrochloric acid. Since spongy particles always separate from the zinc used for the reduction, the solution must be filtered. For this purpose the reduction is carried on in a flask fitted with a long and a short tube, as is a wash-bottle.

¹ The German price lists for 1911 quote about \$1.00 per kilogram.

² Otto von der Pfordten, Liebig's *Annalen*, **228** (1885), 112.

³ *Berichte der deutschen chemischen Gesellschaft*, **41** (1908), 2780.

The longer tube is bent downward above the flask and is here supplied with a small bulb-tube, which is filled with glass-wool or asbestos. The hydrogen given off during the reduction is allowed to pass out through the longer tube for some time; then after closing its outer end the tube is pushed down into the solution. The hydrogen is thus obliged to pass out through the shorter tube, which carries a rubber valve. Carbon dioxide is then passed into the flask through the short tube, and the chromous chloride solution is driven over into a beaker containing a saturated solution of sodium acetate; a red precipitate of chromous acetate is formed which is washed by decantation with water containing carbonic acid. The red chromous acetate is, relatively speaking, quite stable, and in moist condition it may be kept for an unlimited time in closed bottles filled with carbon dioxide.

In washing the red precipitate, some free acetic acid is added in the beginning, to dissolve any basic zinc carbonate which may have been thrown down. In this way a preparation completely free from zinc is obtained.

To absorb oxygen, the chromous acetate is decomposed by the addition of hydrochloric acid, the air being excluded. It is advisable to use an excess of chromous acetate in order to avoid the presence of free hydrochloric acid.

OZONE

Properties of Ozone. — Specific Gravity = 1.62.

Ozone, O_3 , is, at ordinary temperatures, a gas that possesses a peculiar, pungent odor. In a layer one meter thick it shows a distinctly blue color. It has a marked irritating effect on the mucous membrane. It is a powerful oxidizing agent.

The Detection of Ozone. — The detection of ozone, particularly in such small amounts as may be present in atmospheric air, has frequently been the subject of investigation, and many agents and many methods for accomplishing the object have been described in the chemical journals.

It has been found particularly difficult to identify, in the presence of one another, the three gases ozone, nitrogen tetroxide (peroxide) and hydrogen dioxide. This problem appears to have been satisfactorily solved by Keiser and McMaster,¹ who have also given an admirable summary of the earlier work that has been done in this field. For these reasons their article is here quoted in full:

"When air is acted upon in a number of ways, such as by electric sparks, the flaming arc, burning hydrogen, burning magnesium, heated platinum wire, etc., in short, by any means which produce very high temperatures, ozone, nitrogen peroxide, and hydrogen peroxide may be formed. The silent electric discharge and the slow oxidation of phosphorus produce oxidizing gases in air. Several commercial processes of treating air so as to convert it into a more active chemical agent are at present in use. It is desirable, therefore, to have characteristic reactions for each of the three substances above mentioned in examining the gases produced in these different ways.

"A great many reagents have been suggested for this purpose, but many of these have been found to be unreliable, while others are not very sensitive, and still others are rare substances that are not easily obtained. The following table contains a list of such substances, together with a statement of their behavior toward ozone, nitrogen peroxide, and hydrogen peroxide.

	Ozone	Nitrogen peroxide	Hydrogen peroxide
Potassium iodide and starch ²	blue	blue	blue
Wine-red litmus paper moistened with potassium iodide ³	blue	no change	blue
Tetramethylparaphenylenediamine ⁴	bluish violet	bluish violet	bluish violet

¹ *Amer. Chem. J.*, **39** (1908), 96.

² Schoenbein: *Ber. u. d. Verh. d. Nat. Ges.*, Basel, **4**, 58.

³ Houzeau: *Compt. rend.* **45**, 873.

⁴ Wurster: *Ber. d. deutsch. chem. Ges.*, **19**, 3195.

	Ozone	Nitrogen peroxide	Hydrogen peroxide
Metaphenylenediamine, alkaline solution ¹	Burgundy red or yellow	no change	no change
Manganese chloride paper moistened with guiacum tincture ²	blue	blue	no change
Benzidine in alcohol ³	brown	blue	no change
Tetramethyl- <i>p-p</i> -diaminodiphenylmethane in saturated alcoholic solution ⁴	violet	yellow	no change
Potassium ferricyanide and ferric chloride ⁵	no change	no change	blue
Manganese dioxide or copper oxide ⁶	decomposed	no change	decomposed
Silver foil ⁷	black	no change	no change
Chromic acid and ether ⁸ . . .	no change	no change	blue
Chromic acid ⁹	no change		decomposed
Titanium hydroxide in sulphuric acid ¹⁰	no change	no change	yellow
Thallos salts ¹¹	brown	no change	no change
Ammonium molybdate in sulphuric acid ¹²	no change	no change	yellow
Guaiacum tincture with malt infusion ¹³	no change	no change	blue
Gold chloride free from acid ¹⁴ .	black	no change	
Nitrite test with sulphanilic acid and α -naphthylamine ¹⁵ . .	no change	pink	no change

¹ Erlwein and Weyl: *Ibid.*, 31, 3158.

² Engler and Wild: *Ibid.*, 29, 1940.

³ Arnold and Mentzel: *Ibid.*, 35, 1324.

⁴ *Ibid.*

⁵ Schoenbein, Weltzien, also Schoene: *Ibid.*, 7, 1695. Engler and Wild: *Ibid.*, 29, 1940.

⁶ Andrews and Tait: *Ann. Chem. (Liebig)*, 112, 185.

⁷ *Ber. d. deutsch. chem. Ges.*, 35, 1326.

⁸ Barreswill: *Ann. chim. phys.* (3), 20, 364.

⁹ Engler and Wild: *Ber. d. deutsch. chem. Ges.*, 29, 1940.

¹⁰ Schoenn: *Z. anal. Chem.*, 9, 41.

¹¹ Schoene: *Ann. Chem. (Liebig)*, 196, 58.

¹² Schoenn: *Z. anal. Chem.*, 9, 41.

¹³ Struve: *Ibid.*, 8, 315.

¹⁴ Boettger: *Ibid.*, 19, 105.

¹⁵ Bull. Soc. Chim. (3), 2, 347 (1889).

"Arnold and Mentzel¹ have studied a number of the reagents that are mentioned in the preceding list. They find that potassium iodide and starch, and zinc iodide and starch, as well as guaiacum tincture, give a blue color with ozone, nitrogen peroxide, chlorine, and bromine. In short, these reagents are not characteristic of anything more than an oxidizing gas. Red litmus paper moistened with potassium iodide solution they find to be entirely unreliable, because all paper turns blue with free iodine, and any gas that liberates iodine will turn the paper blue. They also found that a solution of potassium iodide to which wine-red litmus solution had been added was unsatisfactory, because the ozone acts upon the litmus and changes it to a green color. The third reagent in the above list, tetramethylparaphenylenediamine, is also turned blue by all oxidizing gases. Metaphenylenediamine, the fourth one, was unsatisfactory because they found that nitrogen peroxide gave the same color as ozone, and all oxidizing gases give yellowish colors with this substance. Silver foil² is not satisfactory because it is not at all sensitive. Arnold and Mentzel recommend an alcoholic solution of benzidine or, still better, an alcoholic solution of tetramethyl-*p-p*-diaminodiphenylmethane. This gives a violet color with ozone and yellow with nitrogen peroxide; with hydrogen peroxide it remains unchanged. They found, however, that the ozone obtained by the action of sulphuric acid upon barium dioxide had a different action upon this reagent; instead of violet a green color was obtained. Benzidine, under the same conditions, gave a blue instead of a brown color. Similar effects were obtained with the ozone from persulphates, percarbonates, and from sodium and hydrogen peroxides.

"F. Fischer and Marx³ have used tetramethyl-*p-p*-diaminodi-

¹ *Ber. d. deutsch. chem. Ges.*, **35**, (1902) 1324.

² Manchot and Kampschulte (*Ber. d. deutsch. chem. Ges.*, **40**, [1907] 2891) have recently shown that while silver foil is not at all sensitive at ordinary temperatures, it becomes much more so at 220°-240° C. For metallic mercury they found the temperature at which action was strongest to be 170° C.

³ *Ber. d. deutsch. chem. Ges.*, **39**, (1906) 2555.

phenylmethane or 'tetramethyl base,' as it is called, in their investigations upon the formation of ozone and nitrogen peroxide in air at high temperatures. They prepared ozone by the silent electric discharge in the Siemen's ozonometer, by the action of ultraviolet light, by the electrolysis of sulphuric acid, and in other ways, and found that ozone produces with this reagent a violet color and the oxides of nitrogen a yellow color. Mixtures of both gases give a dirty brown color intermediate between violet and yellow. Another fact that they emphasize is that the paper must always be kept moist; if it becomes dry, ozone changes it to a yellow color. To detect very small quantities of nitrogen oxides in the presence of ozone they recommend that the gas be conducted into liquid air. The ozone will dissolve while the oxides of nitrogen will separate as blue flakes. When the liquid air is then filtered, the frozen oxides of nitrogen remain upon the filter. The filtrate is allowed to boil, the air distils away, and the ozone remains. In this way both can be separately identified.

"This method is open to the objection that liquid air is not readily obtained in many places. Likewise the 'tetra base' of Wurster and the 'tetramethyl base' of Arnold and Mentzel are not easily obtainable substances. Moreover, the color changes are not always satisfactory. Thallous salts and titanous acid are not always on hand. We have now, however, devised a method which is free from these objectionable features and enables us to identify each of these three substances in the presence of others.

"We found that potassium permanganate, even in very dilute solution, is not decolorized by ozone. Nitrogen peroxide and hydrogen peroxide, on the other hand, both reduce it instantly. To identify ozone in gases that contain at the same time nitrogen peroxide and hydrogen peroxide it is only necessary to draw the gases through a solution of potassium permanganate; the nitrogen peroxide and hydrogen peroxide will not pass through, while the ozone will, and can then be detected with potassium iodide and starch.

“To detect nitrogen peroxide in the presence of ozone and hydrogen peroxide we take advantage of the fact that both ozone and hydrogen peroxide are decomposed when passed through a tube containing powdered manganese dioxide. Nitrogen peroxide passes through unchanged. Its presence can be shown by passing the gas, after it has gone over the manganese dioxide, into very dilute permanganate. If the latter is decolorized, nitrogen peroxide was present. A still more delicate test for nitrogen peroxide is this: pass the gas, which may contain ozone and hydrogen dioxide, directly into pure caustic soda, made from metallic sodium and nitrite-free distilled water, and then test the caustic soda solution for nitrites by the well-known sulphanilic acid and α -naphthylamine method.

“Hydrogen dioxide can be identified in the presence of both ozone and nitrogen peroxide by passing the gas mixture into a solution of potassium ferricyanide and ferric chloride. The yellow brown solution becomes green and then blue as more hydrogen dioxide passes in. This formation of Prussian blue is characteristic of hydrogen dioxide and is not produced by either ozone or nitrogen peroxide. This we have found by experiment.

“**Examination of the Gases Produced by Burning Hydrogen in Air.** — We have tried our method in the examination of the gases produced by burning hydrogen in air. A jet of burning hydrogen was introduced into the end of a glass tube fifteen millimeters in diameter. A current of air was drawn into the tube by means of an aspirator. The gas passed from the tube through a moderately strong solution of potassium permanganate and then into a solution of potassium iodide and starch. This soon became blue, thus showing that ozone was formed by the hydrogen burning in a rapid current of air. The potassium permanganate wash bottle was then replaced by a tube forty centimeters in length, filled with powdered manganese dioxide. Between this tube and the aspirator, a wash bottle with a very weak solution of potassium permanganate was in-

sented. Air was now rapidly drawn through the apparatus and the products of combustion of the hydrogen passed first over the manganese dioxide and then into the dilute permanganate. The latter, after a time, became decolorized, thus showing that nitrogen peroxide was formed. This was confirmed by passing the gases formed by burning hydrogen into a solution of nitrite-free caustic soda and then applying the nitrite test (Griess test) after having slightly acidified the solution. The pink color was formed, thus confirming the result obtained with dilute permanganate. The gases formed by burning hydrogen were also tested for hydrogen peroxide by drawing them through a solution of potassium ferricyanide and ferric chloride. This became first green, then blue, thus showing that hydrogen peroxide was present. This ferricyanide and ferric chloride test for hydrogen peroxide we found to be more sensitive than titanium dioxide in sulphuric acid. The latter failed to show the presence of hydrogen peroxide in the gases produced by burning hydrogen in air.

“Examination of the Gases Produced by the Silent Electric Discharge in Air and Oxygen. — Atmospheric air was purified and dried by being drawn, by means of an aspirator, through a series of wash bottles containing silver sulphate, potassium permanganate, and pure concentrated sulphuric acid, and was then passed through a Siemen's ozonometer. The ozonometer was connected with the terminals of a Ruhmkorff coil which, in turn, was connected with a storage battery. The potential of the coil discharge terminals was 2160 volts. The air passing through the ozonometer in which the silent discharge was taking place was thereupon conducted through a very weak solution of potassium permanganate. No decolorization took place, although the ozonized air was passed for more than two hours. Ozone was shown to be present in quantity, not only by its action upon potassium iodide and starch after it had passed through the permanganate, but also by its odor and by the repeated perforation of the rubber tube that connected the last wash bottle with the aspirator. We were surprised to find that, under these con-

ditions, no nitrogen peroxide was formed. A quantitative determination of the ozone showed that there was 0.00086 gram per liter. We also conducted the air directly from the ozonometer into pure caustic soda and tested this for nitrites by the Griess test but failed to obtain any. With potassium ferri-cyanide and ferric chloride the ozonized air failed to give a reaction for hydrogen peroxide. The same results, namely, the absence of nitrogen peroxide and hydrogen peroxide in air that had passed through the Siemen's ozonometer, were obtained when we omitted washing the air with silver sulphate, caustic soda, potassium permanganate, and sulphuric acid before it entered the ozonometer. These experiments show conclusively that it is possible to ozonize air without, at the same time, forming nitrogen peroxide and hydrogen peroxide. We have repeated the above experiments with oxygen, made from fused sodium peroxide and water, instead of air. We obtained no nitrogen peroxide nor hydrogen peroxide. A quantitative determination showed the presence of 0.0012 gram of ozone to the liter. This ozonized oxygen failed to decolorize potassium permanganate solution.

“Examination of Gases Produced by the Action of Concentrated Sulphuric Acid upon Barium Dioxide. — Concentrated sulphuric acid was allowed to drop upon barium dioxide, contained in an Erlenmeyer flask, and the gases resulting were conducted through a concentrated solution of potassium permanganate in a Geissler potash bulb, and then into a solution of potassium iodide and starch. A blue color soon appeared, thus showing the presence of ozone. The gas, after passing over manganese dioxide and then into permanganate, failed to give the reaction for nitrogen peroxide. Nor were we able to detect hydrogen peroxide by passing the gas through a solution of potassium ferri-cyanide and ferric chloride.

“A small quantity of barium nitrate was now added to the barium dioxide, and, on treating with concentrated sulphuric acid and testing as before, we obtained evidence of the presence

of ozone and nitrogen peroxide, but not of hydrogen peroxide, in the gases given off.

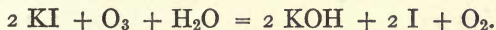
“Examination of the Gases Produced by the Slow Oxidation of Phosphorus in Moist Air. — We have also used our method for the examination of the gases formed by the slow oxidation of phosphorus in air in the presence of water. We found ozone and nitrogen peroxide but no hydrogen peroxide.

“Examination of the Gases Produced by the Action of the Flaming Electric Arc upon Air. — Air that had passed through the flaming electric arc of an Alsop process machine, such as is used in treating flour, was next examined by our method. We found that this air contained nitrogen peroxide, a trace of ozone, and a little hydrogen peroxide.

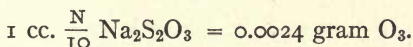
“Examination of Atmospheric Air. — We have applied our method to the examination of country air. Air from outside of the laboratory was drawn through a layer of absorbent cotton, six inches in length, then through a concentrated solution of potassium permanganate in a potash bulb, and finally into potassium iodide and starch. After the air had passed through for five hours, a faint blue color appeared, thus showing the presence of ozone. Air that was filtered through absorbent cotton and that had passed over a layer of manganese dioxide eighteen inches in length was conducted through a very faintly pink solution of permanganate. No decolorization was observed, although the air was drawn through for eighteen hours. We conclude from this that there was no nitrogen peroxide in the air. Air filtered through cotton was drawn through a solution of potassium ferricyanide and ferric chloride. After four hours the solution acquired a green color. We found, however, that the reagent used for detecting hydrogen dioxide, namely, a dilute solution of ferric chloride and potassium ferricyanide, when allowed to stand in air, gradually forms a green precipitate, even when protected from dust by being covered with a bell jar. We, therefore, drew atmospheric air for five hours through pure

distilled water, contained in a potash bulb, and then tested this water with the reagent. We obtained no blue precipitate, and, therefore, conclude that the green color mentioned above may not have been caused by hydrogen dioxide. These experiments prove that our method is sufficiently sensitive to show the presence of ozone in atmospheric air."

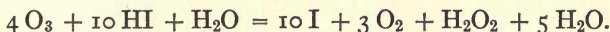
Determination of Ozone. — An excellent method for the determination of ozone is that perfected by Treadwell and Anneler,¹ in which the ozonized oxygen is caused to act upon a neutral solution of potassium iodide,



The liberated iodine is titrated with $\frac{\text{N}}{10}$ sodium thiosulphate after first acidifying the solution with dilute sulphuric acid.



An acid solution of potassium iodide may not be employed because hydrogen dioxide is then formed and this sets free a further amount of iodine.



The gas sample is collected and measured in a bulb of the form shown in Fig. 78, which is a slight modification of that proposed by Treadwell. The bulb, *B*, has a capacity of from 300 cc. to 400 cc. and its volume is accurately determined by weighing it empty and then filled with water, applying correction for temperature.² The carefully ground slip-joint of glass, *A*, serves to connect the bulb with the apparatus from which the ozonized air is to be drawn. Rubber or cork connections may not be used because both are attacked by ozone.

The bulb is filled with distilled water, and the gas sample is drawn in through *A* by opening both stopcocks and allowing the

¹ *Z. f. anorg. Chem.*, 48 (1905), 86.

² See *Analytical Chemistry* by Treadwell, translated by Hall (1911), vol. II, p. 678.

water to flow out. The lower stopcock *H* is then closed, and a few seconds later the upper stopcock *C* is closed. The inlet tube *D* is now removed and the stopcock *C* is opened for an instant to bring the gas to atmospheric pressure. The barometric pressure and the temperature of the room are read and recorded.

The tube below *H* is connected by a piece of rubber tubing with the level-bulb *S* which is then filled with a twice-normal so-

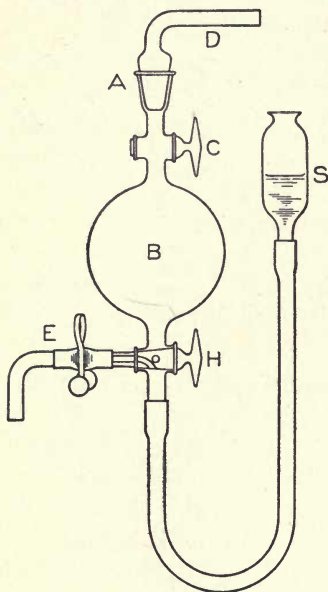


FIG. 78

lution of potassium iodide. Air in the rubber tube is driven out through the end opening of the tail-stopper *H*, and the stopper is then turned and from 20 cc. to 30 cc. of the solution is forced into the bulb. *H* is now closed and the rubber tube is taken off.

The bulb is vigorously shaken and allowed to stand for about half an hour, at the end of which time the absorption of ozone will be complete. The solution in the bulb is then run out into an Erlenmeyer flask, the bulb being rinsed with a small volume of the solution of potassium iodide and then finally with distilled water. The solution is acidified with dilute sulphuric acid and the free iodine

is titrated with a $\frac{N}{10}$ solution of sodium thiosulphate. In computing the per cent of ozone in the gas mixture, the volume v of the gas sample in the bulb is first corrected to the volume v_0 that it would occupy under standard conditions by means of the formula given on page 35. If n

represents the number of cubic centimeters of $\frac{N}{10}$ sodium thio-sulphate used in the titration of the free iodine, then

$$\text{per cent by volume of ozone} = \frac{112 \times n}{V_0}$$

Treadwell and Anneler do not discuss the possibility of interference by nitrogen peroxide or hydrogen peroxide in their method for the determination of ozone nor do they describe any procedure for the removal of these gases. The ozone could probably be freed from the two gases by passing the mixture through a solution of potassium permanganate as recommended by Keiser and McMaster (page 174).

HYDROGEN

Properties of Hydrogen. — Specific gravity, 0.06965; weight of one liter, 0.09004; boiling point, -252° .

According to L. W. Winkler,¹ one volume of water absorbs at

0°,	0.02148	vol. hydrogen
5°,	0.02044	"
10°,	0.01955	"
15°,	0.01883	"
20°,	0.01819	"

At t° alcohol takes up

$$0.06925 - 0.0001487t + 0.000001t^2 \text{ vol. of hydrogen;}$$

hence at

$$20^{\circ}, 0.066676 \text{ vol. (Bunsen).}$$

Detection of Hydrogen. — For the detection of hydrogen Phillips² recommends the use of dry palladious chloride which reacts with hydrogen with the formation of hydrogen chloride that then causes precipitation of silver chloride when the issuing

¹ *Berichte der deutschen chemischen Gesellschaft*, 24 (1891), 89. See also Timofejew, *Zeitschr. für phys. Chem.*, 6 (1890), 141.

² *American Chemical Journal*, 16 (1894), 259.

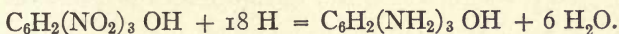
gases are passed through a solution of silver nitrate. Since, however, palladious chloride is reduced by the olefines and by carbon monoxide the method is applicable to the detection of hydrogen only in such gas mixtures as do not contain these constituents. Zenghelis¹ has recently described a method that may be used for the detection of hydrogen in the presence of such hydrocarbons as methane, ethylene and acetylene. It consists in passing the gas mixture through a solution of sodium hydroxide and then through a tube fitted with a tip of platinum foil or platinum wire gauze. The foil or gauze should be carefully ignited before the test is made. This delivery tube is immersed in a few cubic centimeters of a warm solution of sodium molybdate contained in a test tube. The reagent is prepared by dissolving one gram of molybdenum trioxide in dilute sodium hydroxide, adding dilute hydrochloric acid in slight excess and diluting to 200 cc. with water. When molecular hydrogen passes through the delivery tube it is occluded by the platinum and in this condition immediately reduces the ammonium molybdate solution, imparting to the latter an intense blue color. If the amount of hydrogen is very small or if the molybdenum solution is cold, the color is a light greenish blue. Palladium is to be preferred to platinum in testing for hydrogen by this method, but the latter metal gives quite satisfactory results unless there is only a trace of hydrogen in the gas mixture. Arsine, phosphine and carbon monoxide will cause the reduction of the molybdenum solution and consequently these three gases must be removed before the test for hydrogen is made.

Determination of Hydrogen by Absorption.—A method for the volumetric determination of hydrogen by means of a liquid absorbent has recently been described by Paal and Hartmann.² They employ for the absorption of hydrogen gas a solution of colloidal palladium with sodium protalbinat as protective colloid. To avoid the necessity of oxidizing the palladium

¹ *Z. für analytische Chemie*, **49** (1910), 729.

² *Berichte der deutschen chemischen Gesellschaft*, **43** (1910), 243.

hydride after each absorption, they make use of the fact that hydrogen that has been absorbed by colloidal palladium is able rapidly to reduce organic nitro-compounds such as picric acid.



Consequently when sodium picrate is added in excess to the solution of the absorbent, the solution will rapidly and quantitatively absorb a large volume of hydrogen gas.

The authors prepare the reagent by dissolving two grams of sodium protalbinat in 50 cc. of water, adding sodium hydroxide in slight excess and then slowly adding 1.6 grams of palladium chloride (= 1 gram Pd) previously dissolved in 25 cc. of water. A reddish brown liquid results which remains clear. To this is added hydrazine hydrate drop by drop. Reduction takes place at once. The solution is allowed to stand for three hours and is then placed in a dialyzer and dialyzed against water until the outer water shows no further test for hydrazine hydrate or sodium chloride. The resulting solution is concentrated at a temperature of 68° to 70° and is then evaporated to dryness over concentrated sulphuric acid in a vacuum. Black, glistening plates result which are soluble in water without leaving a residue.¹ For the absorption of hydrogen, the authors dissolve 2.74 grams of sodium picrate and 2.44 grams of 61.33% colloidal palladium (Kalle) in water and dilute the solution to 130 cc. The reagent may be used in a Hempel simple gas pipette. Analyses made with this absorbent show that hydrogen is completely removed from a gas sample in from 10 to 30 minutes and that hydrogen may quantitatively be separated from nitrogen and saturated gaseous hydrocarbons. If oxygen is present with the hydrogen in the gas mixture the oxygen should first be removed by means of alkaline pyrogallol or other suitable absorbent because of the fact that colloidal palladium will cause oxygen and hydrogen to unite. Carbon monoxide is not ab-

¹ Colloidal palladium in solid form prepared according to the above procedure may be obtained from Kalle and Company, Biebrich am Rhein, Germany.

sorbed by the reagent, but the gas seems to retard the absorption of hydrogen by colloidal palladium. For this reason the authors recommend that carbon monoxide be first removed by ammoniacal cuprous chloride and that the hydrogen in the residue be then absorbed by the palladium solution.

Brunck has made a careful examination of the method of Paal and Hartmann with a view to ascertaining whether it is adapted to technical practice.¹ He finds that the procedure gives very satisfactory results and states that he regards it as even more accurate than the combustion method for the determination of hydrogen. Brunck employs a Hempel gas burette with water as the confining liquid and a Hempel simple absorption pipette for solid and liquid reagents, see page 55, for holding the absorbent. The removal of the hydrogen is more rapid if the pipette is shaken or if it is filled with small glass balls of from 5 to 7 mm. diameter. The size of these glass balls should be such that when the pipette is filled with them it will still be able to hold from 80 to 90 cc. of gas. The absorbent is prepared either by dissolving two grams of colloidal palladium² in water and adding 5 grams of picric acid that has been neutralized with sodium hydroxide and diluting the whole to from 100 to 110 cc., or by dissolving the corresponding amount of the absorption mixture, which is now prepared ready for use by Kalle and Company, in 100 cc. of water. This amount of the reagent has a theoretical absorbing power of 4369 cc. of hydrogen measured under standard conditions. Relatively small amounts of hydrogen, 10 to 20 cc., are absorbed in about 5 minutes; somewhat larger amounts in about ten minutes. When, however, the gas mixture contains 50 per cent or more of hydrogen, the gas should be passed over into the pipette and allowed to stand for 5 minutes, then drawn back into the burette so that the gas balls in the pipette again become moistened with the absorbent, and

¹ *Chemiker-Zeitung*, 34 (1910), 1313.

² Brunck states that the present market price of this substance in Germany is 10 Marks a gram.

then passed back again into the pipette. This should be continued until no further diminution of gas volume is noted. The removal of hydrogen from 100 cc. of a gas mixture containing a high per cent of this gas takes from 20 to 30 minutes. This method is naturally best applicable to the determination of hydrogen in the presence of nitrogen or of methane, or of both of these gases. A series of analyses of a mixture of hydrogen and nitrogen shows that the determination of hydrogen is accurate to within 0.1 cc. which falls well within the limits of experimental error when the sample is not greater than 100 cc. and the analysis is made over water.

The high cost of the reagent would constitute a serious objection to its employment in technical practice were it not easily possible to regenerate it. This may be done¹ as follows: The reagent is transferred from the gas pipette to a flask and the pipette is rinsed with water which is added to the liquid in the flask. Very dilute sulphuric acid is added drop by drop to the solution so long as a precipitate results. A large excess of sulphuric acid is to be avoided because it might cause the colloidal palladium to change to palladium sulphate through action of atmospheric oxygen. The precipitate which contains palladium, free protalbinic acid and unused picric acid is washed with water which, while it may dissolve some of the acids, carries no palladium into solution. The precipitate is then suspended in a small amount of water and is dissolved by adding sodium hydroxide drop by drop. Fresh sodium picrate is then added, and the solution diluted with water to its original volume of about 100 cc. It is now again ready for use.

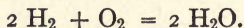
In a recent article² Hempel states that the solution of colloidal palladium foams very strongly and that this necessitates waiting a considerable length of time after the absorption of hydrogen is complete until the foam has disappeared and the gas residue can be transferred to the burette for measurement. He

¹ Paal, *Chemiker-Zeitung*, 34 (1910), 1332.

² *Z. f. angew. Chem.*, 25 (1912), 1841.

cites experiments carried on by Petschek which show that the absorbing liquid prepared according to the method of Paal and Hartmann slowly loses its absorbing power even when it stands in the dark. For this reason Hempel recommends that the reagent be used over mercury in an absorption pipette and that small quantities of the freshly prepared absorbing liquid be employed for the analyses.

Determination of Hydrogen by Explosion.—Hydrogen may be determined by mixing the gas with not more than four times its volume ¹ of pure oxygen, exploding the mixture and measuring the contraction of the gas volume. The gas mixture may be exploded over mercury in a eudiometer such as Bunsen employed, or the explosion pipette described on page 141 may be used. The volume of hydrogen that was present is equal to $\frac{2}{3}$ of the observed contraction



If air is employed instead of oxygen, it should be borne in mind that a mixture of hydrogen and air that contains less than 10 per cent or more than 63 per cent of hydrogen is not explosive ² and that the most accurate results will be obtained when the ratio of the volume of the gas that does not enter into the explosion to that of the hydrogen and oxygen uniting is about 4 to 1. The determination of hydrogen by explosion with oxygen or air is not well suited to technical gas analysis because the reaction is so violent as to necessitate the use of only a small volume of hydrogen with consequent decrease in the accuracy of the results. Moreover, as Misteli points out ³ small amounts of hydrogen escape combustion in the determination of the gas by explosion. Furthermore when nitrogen is present there is possibility of error through the formation of oxides of nitrogen.

¹ Bunsen, *Gasometrische Methoden*, 2d ed., p. 119.

² Teclu, *Journal für praktische Chemie*, 75 (1907), 212.

³ *J. für Gasbeleuchtung*, 48 (1905), 802.

Determination of Hydrogen with Combustion Pipette. —

Hydrogen may be determined with a high degree of accuracy by the combustion method described by the author and C. G. Hopkins.¹ In this method the hydrogen may first be introduced into the combustion pipette (see Fig. 74) and then burned with a mixture of equal parts of oxygen and air, or pure oxygen may be introduced into the pipette and the hydrogen be then passed in. Either procedure gives equally accurate results. In the first form of manipulation a sample (about 100 cc.) of the hydrogen under examination is measured off in a burette and is then passed over into the combustion pipette. A mixture of about equal parts of oxygen and air containing an amount of oxygen more than sufficient for the combustion of the hydrogen is measured off in the burette, and the burette and pipette are then connected by a bent glass capillary tube in the usual manner (see Fig. 75). The platinum spiral is heated to dull redness by means of an electric current, and the mixture of air and oxygen is slowly passed over from the burette into the pipette. During the combustion the current should be regulated by means of the rheostat so that the spiral is at no time heated beyond dull redness. The combustion of the hydrogen is complete almost as soon as sufficient oxygen has been introduced. When nearly all of the mixture of air and oxygen is passed into the pipette, the pinchcock at the top of the burette is closed and the spiral is kept at dull redness for sixty seconds. The current is then turned off, the pipette is allowed to cool and the residual gas is passed back into the burette and measured. In this form of the method the hydrogen is burned with a mixture of oxygen and air because if pure oxygen were used, the contraction in the gas volume in the pipette before an excess of oxygen is introduced would cause the mercury in the pipette to rise and submerge the platinum spiral. The results of a series of determinations of hydrogen made by this method are given in the following table:

¹ *Jour. Am. Chem. Soc.*, 21 (1899), 398.

	I cc.	II cc.	III cc.	IV cc.	V cc.	VI cc.	VII cc.	VIII cc.
Hydrogen taken	99.6	100.0	98.6	99.8	99.4	95.35	97.5	51.15
Oxygen and air added . .	99.6	99.95	99.9	100.0	99.1	96.6	99.75	48.95
Total . .	199.2	199.95	198.5	199.8	198.5	191.95	197.25	100.10
Residue after combustion .	50.0	50.1	50.8	50.55	49.7	49.1	51.2	23.4
Contraction .	149.2	149.85	147.7	149.25	148.8	142.85	146.05	76.7
Equivalent to hydrogen .	99.47	99.9	98.47	99.5	99.3	95.23	97.37	51.13
Hydrogen found	Per ct. 99.9	Per ct. 99.9	Per ct. 99.9	Per ct. 99.7	Per ct. 99.9	Per ct. 99.9	Per ct. 99.9	Per ct. 100.0

In the other style of manipulation a measured amount (about 100 cc.) of oxygen is passed into the combustion pipette, the sample of hydrogen under analysis (about 100 cc.) is measured off in the burette, the burette and pipette are connected, the spiral is brought to dull redness and the hydrogen is slowly passed into the pipette until the following confining liquid reaches the connecting capillary. In either manner of manipulation, the confining liquid, water or mercury, should not be driven further than this because if it were to come in contact with the hot part of the pipette directly over the platinum spiral the glass would probably crack. To insure the complete transferral of the hydrogen from the burette into the pipette the level-tube of the burette is now lowered and about 25 cc. of gas is drawn back into it from the pipette. This is then driven over again into the pipette and the procedure is once more repeated. The spiral is kept at dull redness for sixty seconds longer, the pipette is then allowed to cool and the gas is passed back into the burette and measured.

The Absorption of Hydrogen by Palladium-black (Hempel).—The classic method devised by Hempel for the separation of hydrogen from ethylene, nitrogen and gases of the paraffin series, in which the hydrogen without being mixed with oxygen

is directly absorbed by palladium-black at a temperature of about 100° , is one of the most accurate and satisfactory procedures for the determination of this gas that has ever been devised. The arrangement of the apparatus is shown in Fig. 79. The palladium-black is first rendered active by superficially oxidizing it by heating it to redness on the lid of a platinum crucible and slowly raising the crucible lid out of the flame. About four grams of this palladium-black is placed in the tube *H* which is made of soft glass tubing. This tube has an internal diameter of 4 mm. and is 10 cm. high. To the upper ends of *H* are connected the two bent capillary tubes *D* and *E*. *E* is connected with a gas pipette *C* that contains water, and that is used simply to render possible the passage of the gas back and forth through the palladium-black. The other capillary tube *D* is joined to the burette *A* that contains the gas mixture in which free hydrogen is to be determined. Gases other than hydrogen, nitrogen, ethylene, and methane and its homologues must previously be removed by absorption. There is now brought up under the U-tube *H* a beaker containing water at a temperature of about 100° . The point at which the water stands in the capillary of the pipette is noted, the pinchcock *P* is then opened and the gas mixture passed three times back and forth through the palladium tube by raising and lowering the level-tube *B*. The beaker of hot water is now replaced by one containing water of the temperature of the room and the gas residue is twice passed back and forth through this tube to cool it. The gas is then drawn back into the burette until the water stands at the original point in the capillary of the pipette. *P* is then closed and the residual gas volume in the burette is measured. The difference between the measurements made before and after the absorption is equal to the hydrogen in the gas mixture plus the volume of the oxygen in the air that was originally inclosed in the U-tube when the apparatus was put together.

This volume of oxygen in the U-tube may accurately be determined once and for all in the following manner. Somewhat

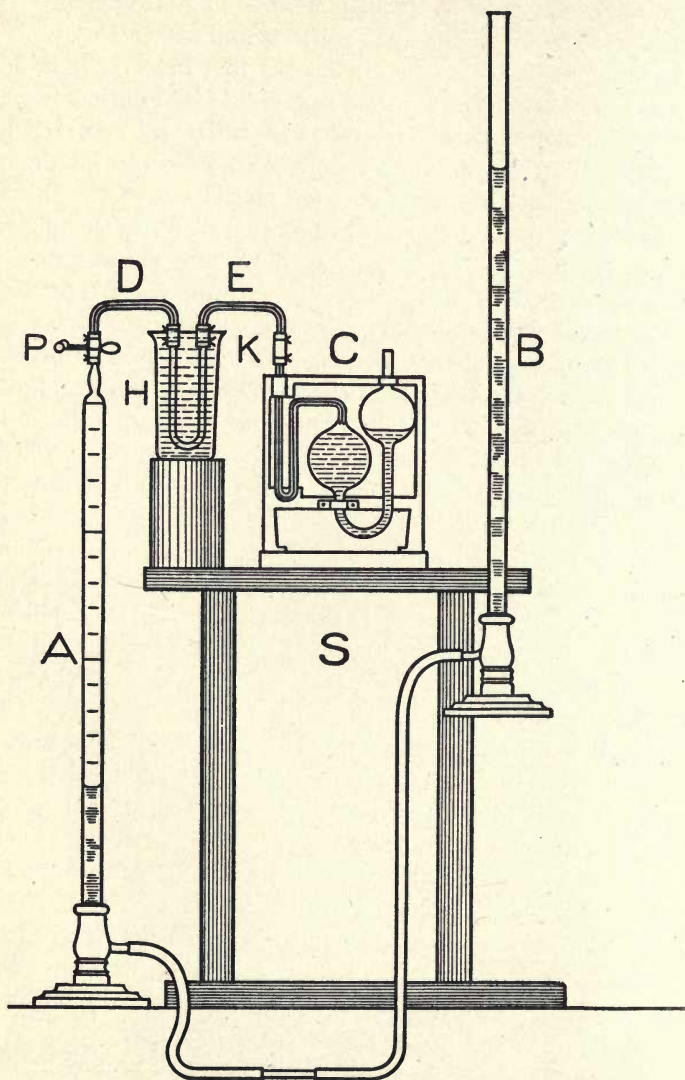


FIG. 79

more than 100 cc. of air is drawn into a phosphorus pipette (Fig. 35) and allowed to stand until the oxygen has been removed and the fumes of phosphorus pentoxide have been absorbed. The pipette is connected with a gas burette and the nitrogen in the pipette is passed over into the burette and is measured. The pipette is now connected with one end of the freshly filled palladium tube which itself is immersed in a beaker of water of the temperature of the room. The other end of the U-tube is connected with the burette that contains the nitrogen. The level-tube of the burette is then raised and the nitrogen is driven over into the pipette until the confining liquid reaches the top of the burette. The pinchcock is then closed and the gas is allowed to stand in the phosphorus pipette for about three minutes. The gas is then drawn back into the burette and again passed over into the pipette. The residual nitrogen is then drawn back into the burette and its volume is read. The difference between this and the first reading gives the volume of oxygen that was originally in the palladium tube. The palladium-black is regenerated from time to time by heating it on the lid of a platinum crucible in the manner above described.

The Fractional Combustion of Hydrogen. — In the analysis of those mixtures of gases that most commonly occur in technical practice, the determination of the majority of the constituents may be accomplished by the absorption of the gases by liquid reagents or by solid reagents immersed in liquids. This method is, however, not applicable to the determination of the gases of the paraffin series nor has it been possible until recently (see page 182) to remove hydrogen by means of a liquid absorbent. In gas mixtures or gas residues that contain hydrogen and only one member of the paraffin series, both gases may satisfactorily be determined by burning the gases simultaneously in the combustion pipette shown in Fig. 74, measuring the contraction, and ascertaining the volume of carbon dioxide that has been formed. The analysis of such a mixture of combustible gases by the explosion method (see page 141) is not as accurate as that by the

combustion method just referred to. Particularly is this true of the simultaneous determination of hydrogen and methane in gas residues that contain large amounts of these two gases, for in such case only a small portion of the combustible residue can safely be exploded and consequently any experimental error is multiplied five- to eight-fold when the results are calculated for the whole of the gas residue. Moreover, if two or more hydrocarbons of the same group are present with the hydrogen, the gases cannot be determined by any combustion or explosion method in which all of the combustible gases are simultaneously burned (see page 131). For these reasons a satisfactory method for the fractional combustion of mixtures of hydrogen and hydrocarbons of the paraffin group, a method by means of which the hydrogen gas alone may be burned without oxidation of the hydrocarbons, has long been sought and many different procedures have been suggested.

Fractional Combustion of Hydrogen with Platinum or Palladium Asbestos. — The first method of fractional combustion was proposed by Henry ¹ who found that he could remove hydrogen and carbon monoxide from the mixture of these two gases with methane and nitrogen by passing the gases over platinum sponge heated to 177°. Somewhat later Coquillion discovered ² that hydrogen and methane, when mixed with air, could be burned by passing the gases over a spiral of metallic palladium heated to bright redness by an electric current. In 1878 Bunte described ³ a method for the combustion of hydrogen in which the mixture of the gas with air or oxygen is passed over palladium that is heated externally to the desired temperature by means of a small flame. It was afterward found that if the temperature to which the metallic palladium is heated is kept below a certain point, methane does not burn and that consequently the determination of hydrogen when admixed with methane may be

¹ *Annals of Philosophy*, 25 (1825), 428.

² *Compt. rend.*, 83 (1876), 799; 84 (1877), 1503; 85 (1878), 1106.

³ *Berichte der deutschen chemischen Gesellschaft*, 11 (1878), 1123.

effected in this manner. Other contact substances for the fractional combustion of hydrogen have been suggested.¹ In later articles upon this subject, different authors called attention to the fact that some or all of the methane will burn with the hydrogen if the temperature is allowed to rise too high, but considerable difference of opinion existed as to the temperature to which the catalytic substance might be heated without causing oxidation of the methane. In fact, in many of the published methods, the authors contented themselves with a description of some arbitrary method of heating the tube containing the catalyzer and evidently assumed that when the conditions that they laid down are followed, no methane will be burned. For example, in the instructions given by different writers concerning the heating of the glass tube containing palladium wire or palladium asbestos are to be found such statements as the following: "the heating of a tube should be gentle and in no case should it cause a visible glow:" "the tube should be heated to such a temperature that it can be touched for a moment without burning the finger:" "the tube should be heated to such a temperature as will just be sufficient to cause the potassium or sodium in the glass to color the Bunsen flame." It is true that the last statement was made by a writer who ascertained by means of a thermocouple that the difficultly fusible glass tubing that he was using began to color the Bunsen flame at a temperature lying between 550° and 600°, but his directions would be of dubious value to another operator using a different sample of hard glass. Moreover, as Richardt has pointed out,² finely divided contact substances such as palladium asbestos, platinum asbestos or palladium sponge are poor

¹ Palladium asbestos, Winkler, *Anleit. z. chem. Unters. der Industrie-Gase*, part 2, p. 258.

Palladium sponge, Hempel, *Berichte der deutschen chemischen Gesellschaft*, 12 (1879), 1006.

Platinum asbestos, Kopfer, *Berichte der deutschen chemischen Gesellschaft*, 9 (1876), 1377.

² *Z. f. anorg. Chem.*, 38 (1904), 65.

heat-conductors, and for this reason the heat developed by the combustion of the gases within the tube may locally raise the catalyzer to a temperature at which methane will burn, even when the external heating of the tube is very carefully regulated. The observation of Winkler¹ that even when the glass capillary tube containing palladium asbestos is very carefully heated by a small gas flame "the end of the asbestos thread against which the entering current of gas impinges is heated to a bright glow, and that this glow is frequently again seen when the gas sample is passed back into the burette" is one that is familiar to all who have used this method of fractional combustion.

To ascertain the temperature at which methane, when mixed with air, will be oxidized upon passage over a catalytic agent Richardt² passed the gas mixture over palladium wire that was placed in a capillary tube which was heated from the outside by a small flame. He employed palladium wire instead of palladium asbestos because the compact metal, having high heat conductivity, rendered it possible to avoid local superheating. He found that methane was oxidized to some extent at a temperature but slightly above 450° and that it rapidly burned at temperatures above 700° . From these measurements it is evident that if the catalytic substance is heated to a dull red glow that is visible in daylight, which according to Richardt corresponds to a temperature from 750° to 800° , combustion of some of the methane will undoubtedly result.

Results confirmatory of the statements of Richardt were later obtained by Denham³ who found that the temperature of combustion of practically pure methane and oxygen when the gas mixture is passed through a tube containing palladium asbestos lies between 514° and 546° .

Brunck maintains⁴ that the results obtained in the fractional

¹ *Lehrbuch der technischen Gasanalyse*, 1901, 168.

² *Loc. cit.*

³ *J. Soc. Chem. Ind.*, 24 (1905), 1202.

⁴ *Z. f. angew. Chem.*, 16 (1903), 695.

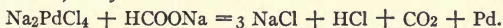
combustion of hydrogen by means of palladium asbestos are accurate even when the asbestos thread visibly glows during the passage of the gas mixture, but even his own confirmatory analyses show that with slight elevation of the temperature of the capillary tube, some methane is oxidized. If the palladium asbestos glows during the passage of the gas its temperature is undoubtedly considerably above 500° . With this fact in mind it is difficult to reconcile the statements of Brunck with the experimental results of Nesmjelow¹ which appear to demonstrate that when a mixture of hydrogen, methane and air is passed through a capillary tube that contains palladium asbestos an appreciable amount of methane is oxidized at 150° . It is certainly the case that when the fractional combustion of hydrogen by means of palladium asbestos is carried out in the manner prescribed in almost all of the various descriptions of the method, the temperature of 150° will be greatly exceeded, particularly when a porous catalyzer is employed.

In a recent review² of this method Hempel finds that hydrogen may be determined with accuracy in the presence of methane and ethane if the palladium asbestos does not glow during the analysis, and if the temperature of the capillary itself does not rise appreciably above 400° . He states that this may be accomplished by heating the capillary in a certain manner, which he describes, and by passing the gas mixture very slowly through

¹ *Z. f. analytische Chemie*, **48** (1909), 232.

In this article Nesmjelow gives the following directions for the preparation of palladium asbestos:

Dissolve three grams of sodium palladious chloride in as small an amount of water as possible, add three cc. of a cold, saturated solution of sodium formate, and then sodium carbonate to strong alkaline reaction. Place in the solution one gram of long-fibered, soft asbestos which will absorb practically all of the liquid. Dry the fiber on the water-bath. Metallic palladium will hereupon separate evenly on the asbestos in a black, finely divided form:



After complete drying on the water-bath, the asbestos is softened with water, and then is placed in a funnel and washed with warm water until the adhering salts are removed. It is then dried and kept in stoppered glass bottles.

² *Z. f. angew. Chem.*, **25** (1912), 1841.

the tube, and that if these directions are followed *with the greatest care* the method gives agreeing results. These statements by Hempel serve to accentuate the uncertainty inherent in the fractional combustion of hydrogen by means of a catalytic substance that is heated with a free flame, and they render it evident that slight variations in the procedure may easily give rise to errors of considerable magnitude.

A much more satisfactory procedure for the fractional combustion of hydrogen is Hempel's method of burning the hydrogen by means of palladium black that is kept at a temperature below 100° , or that of Jäger in which the fractional combustion of the hydrogen is accomplished by passing the gas over copper oxide at a temperature of 250° .

Fractional Combustion of Hydrogen with Palladium Black (Hempel). — The method is based upon the fact that if a mixture of hydrogen, methane and air, oxygen being present in excess, is passed over palladium black at a temperature not above 100° , hydrogen alone is burned.

Finely divided palladium is prepared for use in this method by heating it to redness upon the lid of a platinum crucible and gradually removing it from the flame so that it will cool slowly. This covers the metal with a very thin layer of palladious oxide.

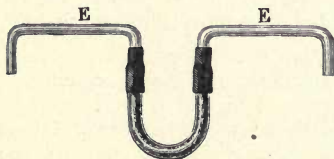


FIG. 80

About 0.5 gram of this palladium black is placed in a small U-shaped glass tube (Fig. 80). This tube is connected by short pieces of rubber tubing with the bent capillary tubes *EE* one of which is joined to a gas burette while the other is connected

with a simple gas pipette filled with water.

From 15 to 20 cc. of the mixture of hydrogen and methane is brought into a Hempel burette and accurately measured. There is then drawn into the burette such an amount of air as will insure the presence of more than enough oxygen to unite with

the hydrogen in the gas mixture. The total volume of the gas is now measured. The right hand capillary *E* having been connected with a gas pipette filled with water, the left hand capillary is now joined to the burette containing the gas sample and air, and a beaker containing water of a temperature of from 60° to 80° is brought up under the U-shaped tube and set at such a height that the water stands just below the lower ends of the rubber connections. The gas mixture in the burette is now passed *very slowly* through the palladium tube into the pipette. With too rapid a passage of the gas mixture over the palladium black the heat developed by the combustion of hydrogen may raise the palladium to a temperature at which methane will begin to burn. With reasonable care, however, the temperature of the U-tube and of its contents may easily be kept below 100° and the combustion of methane entirely avoided. The gas mixture is passed backward and forward from burette to pipette until no further decrease in the volume of the gas is observed. The beaker of warm water is then removed and is replaced by a beaker filled with water of the temperature of the room. When the residual gas has in this manner been brought to room temperature, the diminution of the volume of the gas is read. The volume of hydrogen in the sample is equal to two-thirds of the contraction noted. Hempel gives the following results as confirmatory of the accuracy of this method.

COMPOSITION OF THE GAS MIXTURE			RESULTING CONTRACTION	HYDROGEN CALCULATED FROM THE CONTRACTION
Hydrogen	Marsh-gas	Air		
1.5	12.0	85.1	2.3	1.5
3.0	8.3	86.5	4.5	3.0
5.1	12.3	86.0	7.6	5.0
9.3	7.1	83.7	14.1	9.4
13.7	7.3	77.5	20.3	13.5
14.1	5.4	81.2	21.2	14.1
14.6	4.5	80.6	22.1	14.7
13.1	6.0	80.3	19.7	13.1

An objection that may, however, be urged against this method is that only a portion of the combustible residue is employed and consequently an experimental error in the combustion is multiplied several times when the result is calculated for the total residue.

Fractional Combustion of Hydrogen with Copper Oxide (Jäger). — The use of copper oxide for the determination of gaseous hydrocarbons was proposed by Fresenius as long ago as 1864,¹ and the method was afterward further developed by Scheurer-Kestner² and Stöckmann.³

Jäger was the first who proposed the use of copper oxide in the *fractional* combustion⁴ of hydrogen in the presence of methane, hydrogen being completely burned when passed over copper oxide⁵ at a temperature of 250°, whereas methane is not oxidized at all under these conditions. Jäger places copper oxide in a hard glass tube 6 cm. in length and one cm. in external diameter. One end of the tube terminates in a straight capillary tube 3 cm. long. To the other end is fused a glass tube 4 cm. in length and 5 mm. internal diameter through which the fine granular copper oxide is introduced. This combustion tube is connected on one side to a gas burette and on the other to a Hempel simple gas pipette containing a solution of potassium hydroxide. To facilitate the control of the temperature the combustion tube rests in a small oven of sheet iron through the top of which a thermometer is inserted to such a distance that its bulb rests directly

¹ *Z. f. analytische Chemie*, 3 (1864), 339.

² A. Scheurer-Kestner, *Bullet. de la Societe industrielle de Mulhouse*, 1868; *Civil-ingenieur*, N. F., XV, 123.

³ C. Stöckmann, *Die Gase des Hochofens und der Siemens-Generatoren*, Ruhrort 1876, 6.

⁴ *Jour. f. Gasbeleuchtung*, 41 (1898), 764.

⁵ The oxygen for the combustion of hydrogen comes from the solid copper oxide which on reduction decreases in volume. Consequently the results obtained by measuring the contraction of the gas volume are somewhat too high. The error from this source is, however, so very small that it may be entirely disregarded. For example, in the determination of hydrogen, the correction would be 0.00047 cc. for each cubic centimeter of the gas.

against the combustion tube. The oven is heated from below by a single gas burner. In the fractional combustion of hydrogen in a mixture of that gas with methane and nitrogen the combustion tube is first heated to 250° , and the gas mixture is then slowly passed through it from the burette into the pipette. Jäger found that a double passage of the gas through the tube usually suffices for the complete combustion of the hydrogen, but the gas mixture is usually passed through the tube a third time to ascertain whether further diminution in volume takes place. Since the oxygen of the air that is originally contained in the combustion tube burns with the hydrogen, the contraction due to this source must be ascertained. Jäger does this once and for all by passing through the heated combustion tube a mixture of known volumes of hydrogen and nitrogen. The observed contraction less the contraction due to the hydrogen used gives the volume of the oxygen in the combustion tube.

The method is distinctly superior to the fractional combustion of hydrogen by palladium or palladium asbestos because—

1. No air or oxygen is added to the combustible gas, which makes it possible to pass the total gas residue through the tube with consequent gain in accuracy of the analytical results:

2. The temperature at which the hydrogen burns, 250° C., is so easily controlled and is so far below the temperature at which methane will be oxidized as to render impossible the combustion of any of the methane;

3. The material and apparatus are inexpensive.

To avoid the necessity of determining the volume of oxygen in the combustion tube and of making correction for it, v. Knorre¹ first fills the tube with nitrogen, this gas being passed into the combustion tube through a T-tube that is introduced between the combustion tube and the pipette. He obtains the necessary volume of nitrogen by passing air into a phosphorus pipette (page 164) and he states that the nitrogen residue from

¹ *Chemiker-Zeitung*, 33 (1909), 717.

100 cc. of air is amply sufficient to displace the oxygen in the combustion tube.

Jäger recommended that the methane in the gas residue be determined, after the fractional combustion of hydrogen, by raising the temperature of the combustion tube to bright redness, passing the mixture of methane and nitrogen through the tube and ascertaining the volume of methane by determining either the contraction or the volume of carbon dioxide formed in the combustion. Methane, however, is not easily burned by passage over hot copper oxide and complete combustion of the gas is effected only by repeatedly passing it through the combustion tube. Moreover, since the tube itself must be kept at a bright red heat throughout the process, it frequently softens and if a drop of water enters it, it instantly breaks. These difficulties in the determination of methane are avoided by v. Knorre by substituting for the hard glass tube a tube of transparent quartz 15 cm. long, 5 mm. internal diameter and with a thickness of wall of from 0.5 to 0.75 mm.

Ubbelohde and de Castro¹ also use a quartz tube filled with copper oxide which they heat to 270° for the combustion of the hydrogen, and then to bright redness (800° to 900°) to burn the methane and ethane. In the latter combustion they heat the quartz tube with a free flame and place a clay trough over the tube to bring the temperature to the highest point possible.

Excellent as is the Jäger method for the accurate determination of hydrogen, the subsequent combustion of methane at a higher temperature in the same tube cannot unqualifiedly be recommended. If hard glass is used for the combustion tube, the tube must either be ordered from a glass blower or the chemist who makes his own simple glass apparatus must purchase both small tubing and capillary tubing of hard glass for fusion to the ends of the combustion tube proper. The glass tube is also apt to break when heated or when water is carelessly allowed to enter it during the combustion. The quartz tube is

¹ *J. f. Gasbeleuchtung*, 54 (1911), 810.

more durable, but apparatus of transparent quartz is fragile and expensive and, in this country at least, it cannot as yet readily be obtained. The chief objection, however, to this method of determining methane lies in the fact that prolonged heating of the combustion tube to a high temperature and repeated passage of the gas through it are necessary for the complete oxidation of the methane. Because of these considerations the author deems it preferable to restrict the combustion with copper oxide to the fractional combustion of hydrogen, and to determine the residual methane by combustion with oxygen in the Dennis combustion pipette. Since the combustion tube need be heated only to 250° if hydrogen alone is to be burned, this modification of the procedure makes it possible to use a tube of soft glass which can easily be blown by the operator himself. The subsequent determination of methane by means of the combustion pipette is fully as accurate as the combustion with copper oxide and is much more rapid. The following arrangement and manipulation of apparatus have been found to give very satisfactory results.

The combustion tube (Fig. 81) is made of soft glass throughout. It consists of a piece of glass tubing *H*, 7 cm. long, 12 mm. external diameter, and one mm. thickness of wall; to one end of this tube is fused a piece of glass tubing 6 cm. long and 7 mm. external diameter; to the other end is fused a piece of capillary tubing of the dimensions used in the Hempel pipettes, namely, 6 mm. external diameter and one mm. internal diameter, which is then bent at a right angle as shown in the figure. *H* is filled through the wide end with granular copper oxide which is held in place by a loose plug of ignited asbestos. Inasmuch as the temperature of the copper oxide during the combustion should be kept nearly constant at 270° , the combustion tube is not heated with a free flame, but is placed in a small air-bath, *J*. Ubbelohde and de Castro employ an oven made of sheet iron and lined with asbestos, and fitted with two perforated iron plates for the even distribution of the heat. A device that is

simpler and fully as satisfactory may be constructed in the laboratory from ordinary asbestos board. A piece of asbestos board 9 cm. wide, 30 cm. long and 6 mm. thick is creased at

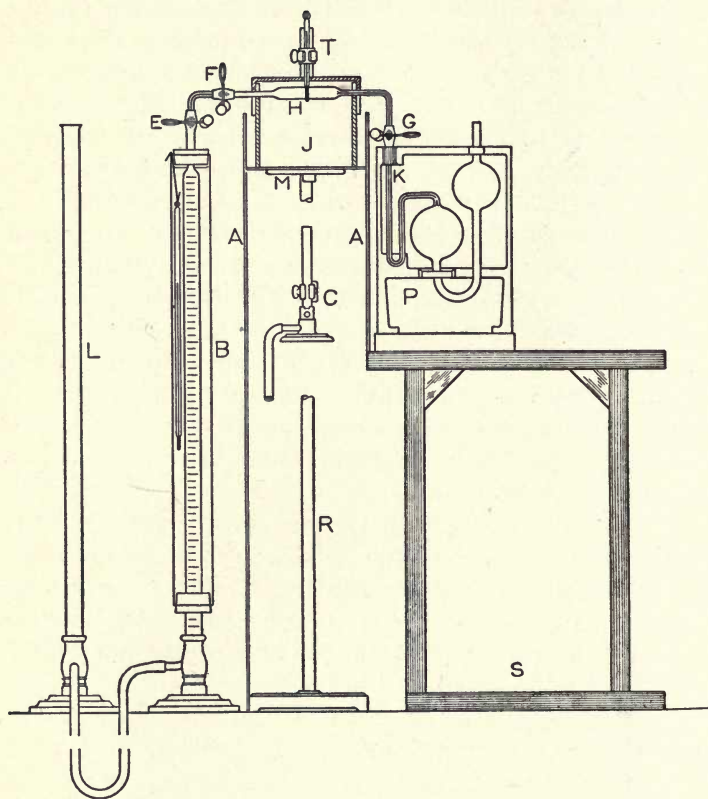


FIG. 81

points about 7.5 cm. apart, bent into a four-sided form and the ends connected by shaving one down to a sharp edge, splitting the other, inserting the narrow edge in the split end and then thoroughly wetting the asbestos and pressing it together. The two opposite sides of this box are notched to a depth of about

4.5 cm. and the small combustion tube rests in these notches. The box, which is open at the bottom, rests upon a piece of sheet iron that is supported on an iron ring, *M*. An asbestos top, with sides 6 cm. high, is made from asbestos board in the same manner and opposite sides of the top are notched so that the top will set down over the box and completely close it except where the combustion tube passes through. A small opening in the top made with a cork borer serves for the introduction of the thermometer *T* which is placed in such position that its bulb rests against the side of the combustion tube. The air bath is heated by a single Bunsen burner, *C*. A flame about 6 cm. high suffices to keep the interior of the box and the combustion tube at a temperature of 270° .

Although the little asbestos oven is not heated higher than the comparatively low temperature of 270° throughout the determination it is advisable for the protection of the burette and the pipette to place strips of asbestos board, *AA*, about 15 cm. wide, between the pipette and the oven on the one side and the oven and the burette on the other.

In making a determination of hydrogen with this apparatus the combustion tube is placed in position in the asbestos box, and its left-hand end, Fig. 81, is connected with a water-jacketed Hempel burette that contains water¹ as the confining liquid and that has previously been filled with nitrogen from a phosphorus pipette.

¹ Mercury may of course be used as the confining liquid, and a burette with correction tube and manometer may be employed if great accuracy is desired. In technical practice, however, results that are correct to within one-tenth of one per cent are usually sufficiently accurate, and inasmuch as the manipulation of the apparatus is more simple and more rapid when water is used as the confining liquid instead of mercury, the method here described for the determination, over water, of not only hydrogen but of methane as well, has been worked out for the convenience of the general analyst. If methane is the only hydrocarbon that is present with the hydrogen, the two gases may more rapidly be determined by the simultaneous combustion of both with the combustion pipette, but in such case mercury must be used as the confining liquid in both burette and pipette. Furthermore, if two members of the paraffin group (e. g., methane and ethane) are present in the gas residue after the hydrogen has been removed by fractional combustion with copper oxide, the

The pinchcock *E* at the top of the burette is opened and the nitrogen is passed through the combustion tube into the outer air. This washes out the air in the combustion tube, and frees it practically completely from all oxygen. The pinchcock *E* of the burette is closed and a simple gas pipette filled with water up to the top of the rubber connecting tube at *G* is at once joined to the combustion tube.

The rubber tube on the other end of the combustion tube is now closed by the pinchcock *F*, the burette is disconnected from the bent capillary tube and about 100 cc. of the gas mixture under examination, which should of course previously have been freed from all gases except hydrogen, nitrogen and members of the paraffin series, is drawn into the burette and measured. While this is being done the heating of the asbestos oven surrounding the combustion tube is begun and the pinchcock *F* is opened for a moment from time to time to relieve the excess pressure due to the expansion of the nitrogen in the tube. The heating is continued until the thermometer shows a temperature of 270° and the tube is kept at about this temperature during the combustion. The pinchcock *F* is then once more opened to bring the nitrogen in the combustion tube to atmospheric pressure and the burette is then connected with the bent capillary tube. The pinchcocks *E*, *F* and *G* are now opened and the gas mixture in the burette is *slowly* passed through the combustion tube into the water pipette. If the gas is passed through the tube at the rate of about 10 cc. per minute it has been found that four or five passages of the gas will completely remove the hydrogen from 100 cc. of a gas mixture that contains 40% of this gas.

two paraffins can be determined in the combustion pipette only when mercury is used as the confining liquid. In gas analysis, as in any other line of analytical work, it should constantly be borne in mind that the refinements of a method should be in accord with the accuracy that is desired. In the present instance, if results that are correct to within about one-tenth of one per cent meet the needs of the case, it would involve useless consumption of time to employ a very accurate gas burette and to measure the gases over mercury. On the other hand, if great accuracy is desired, it would be folly to attempt to attain it by measurement of gas volumes over water.

With a higher percentage of hydrogen, or in fact in any case, the gas should be passed backward and forward through the combustion tube until two successive readings are the same. After the removal of the hydrogen is completed, the gas is drawn back into the burette until the water in the capillary of the pipette stands just above *K*. The pinchcock *G* is then closed. The temperature of the combustion tube is now brought again to exactly 270° by raising or lowering the Bunsen flame, and the pinchcock *E* is closed. The gas is allowed to stand in the burette for two minutes to come to the temperature of the surrounding water and its volume is then read. The contraction in volume shows directly the amount of hydrogen.

If it is desired to determine methane in the gas residue in the burette, the water pipette is replaced by a combustion pipette (Fig. 74) that is filled with water ¹ and that contains a measured amount of oxygen, about 100 cc. The terminals of the pipette are connected with a source of electric current, the current is turned on, and the spiral is heated to dull redness. The combustion tube *H* is kept at about 270° . The level-bulb of the pipette is placed upon the top of the stand *S*. A Hofmann detachable screw pinchcock is placed upon the rubber tube that connects the burette with its level-tube; the level-tube of the burette is then brought to such height that the confining liquid in it stands but slightly higher than the confining liquid in the burette, and the screw pinchcock is now closed. The level-tube is placed upon the top of another wooden stand like *S*. The pinchcocks *E*, *F*, and *G* are opened and set back on the glass tubes. The screw pinchcock is then very carefully opened, and the gas in the burette is very slowly started over through *H* into the combustion pipette. When the water in the burette has risen to the top of the burette, the pinchcocks *E*, *F*, and *G* are closed, and the burette is disconnected from the small capillary tube at *E*. The burette is then connected to a phosphorus pipette containing nitrogen and a known volume, from 15 to

¹ Mercury may of course be used.

20 cc., of nitrogen is drawn into the burette. The burette is then disconnected from the phosphorus pipette and is again connected to the small capillary at *E*. Pinchcocks *E*, *F*, and *G* are opened, and the gas forced from the burette through the tube *H* into the combustion pipette as before. When the water in the burette reaches the top of the burette, pinchcock *E* is closed, and the tube *H* is again brought to exactly 270° C. The gas in the combustion pipette is now brought to atmospheric pressure by proper adjustment of the height of the level-bulb of the pipette and the pinchcock *G* is then closed. The burette and the combustion pipette are disconnected from the tube *H*, and the burette is joined directly to the combustion pipette by a capillary tube of the usual form. The gas is drawn from the combustion pipette into the burette and is then passed into a pipette containing a solution of potassium hydroxide to remove carbon dioxide. The residual gas is now brought back into the burette, and is again measured. To ascertain the volume of methane in the sample, add the volume of gas remaining after the determination of hydrogen to the sum of the oxygen introduced into the combustion pipette and the volume of nitrogen used for sweeping the residual gas out of the tube *H*. From this sum, deduct the final volume of the gas that remains in the burette after the absorption of the carbon dioxide formed in the combustion of the methane. One-third of this result is the volume of the methane in the gas sample.

NITROGEN

Properties of Nitrogen. — Specific gravity, 0.9701. Weight of one liter, 1.2542 grams.

Nitrogen is but slightly soluble in water, one volume of water absorbing, according to Bunsen, at 760 mm. pressure and *t*°,

$0.020346 - 0.00053887 t + 0.000011156 t^2$ vol. of nitrogen:
or at

5°	0.01794	vol.
10°	0.01607	"
15°	0.01478	"
20°	0.01403	"

Otto Pettersson and K. Sonden¹ state that at a pressure of 760 mm. 1 liter of water absorbs from the air: —

at	0°, 19.53	cc.
"	6°, 16.34	"
"	9.18°, 15.58	"
"	14.10°, 14.16	"

According to Carius, one volume of alcohol takes up at t° ,

$$0.126338 - 0.000418 t + 0.000006 t^2 \text{ vol. of nitrogen;}$$

hence at

$$20^\circ, 0.122378 \text{ vol.}$$

Absorption of Nitrogen. — In the analysis of gas mixtures the residue that cannot be determined by the usual absorption methods or by combustion was earlier regarded as consisting wholly of nitrogen and is still commonly reported as such. From the researches of Rayleigh and Ramsay we now know that this residue frequently contains, in addition to nitrogen, one or more of the gases of the argon group, which consists of argon, neon, krypton, xenon and helium. In the earlier work in this field, nitrogen was separated from the gases by passing the gas mixture over hot magnesium, lithium, or a mixture of magnesium and calcium oxide, any of which agents unite with the nitrogen but do not affect the gases of the argon group.

To obtain information as to the relative efficiencies of these various absorption agents, Hempel placed the different substances in hard-glass tubes, exhausted these tubes of air, and then introduced an excess of nitrogen. The tubes were then heated to bright redness, the nitrogen was pumped out and

¹ *Berichte der deutschen chemischen Gesellschaft*, 22, (1889), 1443.

measured, and the amount of that gas which had been held back by each absorbent was thus determined.

The results were as follows:—

ABSORPTION AGENT EMPLOYED	Number of Cubic Centi- meters of Ni- trogen that was absorbed in fifteen minutes	Number of Cubic Centi- meters of Ni- trogen that was absorbed in one hour
1 gram magnesium powder, medium fine . . .	—	14.5
1 gram lithium . . .	—	73.5
1 gram magnesium and 5 grams quicklime. The lime was not freshly ignited . . .	94.5	112.0
1 gram magnesium and 3 grams quicklime. The lime was not freshly ignited . . .	—	50.0
1 gram magnesium and 8 grams quicklime. The lime was not freshly ignited . . .	—	31.4
1 gram magnesium and 5 grams quicklime. The lime was highly ignited shortly before the experiment . . .	86.4	122.5
1 gram magnesium, 5 grams freshly ignited lime, and 0.1 gram metallic sodium . . .	201.0	287.0
1 gram magnesium, 5 grams freshly ignited lime, and 0.25 gram metallic sodium . . .	196.0	326.2
1 gram magnesium, 5 grams freshly ignited lime, and 0.11 gram metallic lithium . . .	169.0	228.0

Ignited lime with metallic sodium alone absorbed no nitrogen whatever, and only very slight absorption is effected by barium carbide alone, barium carbide and potassium, barium fluoride and sodium, or amorphous boron and silicon. It is possible that the barium carbide used in these experiments decomposed partially when it was pulverized.

From these experiments it appeared that, of the substances tried, the best absorbent for nitrogen is a mixture of one part by weight of finely powdered magnesium with five parts by weight of freshly ignited lime in pieces about as large as poppy seeds, and 0.25 part by weight of metallic sodium. The magnesium should be intimately mixed with the ignited lime, but it is sufficient to add the sodium in the form of a number of pieces

each about half as large as a pea. The layer of oxide covering the metallic sodium should first be removed, and the metal should be added to the mixture just before using.

The "analytical absorbing power" of the mixture, based upon the amount of the magnesium, is 8.15 cc.

Magnesium and lime react to form metallic calcium. Since the above experiments were made, metallic calcium has come upon the market, and this may now be used directly for the removal of the nitrogen, instead of being formed within the apparatus by the interaction of magnesium and lime. Metallic calcium energetically combines with nitrogen forming calcium nitride, Ca_3N_2 .

The researches of Franz Fischer¹ have demonstrated that calcium carbide may be employed for the absorption of nitrogen and also for the simultaneous removal of oxygen.

To remove nitrogen from a mixture of this gas with the gases of the argon group, the gas mixture, after having been freed from other constituents, may be driven backward and forward by means of mercury through a heated tube containing one or another of the above absorbents. Constant raising and lowering of the mercury level-bulbs is, however, a tedious procedure, and for this reason, if any appreciable amount of nitrogen is to be removed, it will be found convenient to employ the Travers² modification of the automatic device described by Collie.³ By means of this apparatus the gases can automatically be driven through the absorption apparatus in a continuous current. Fig. 82 shows an arrangement of the apparatus substantially in the form recommended by Travers except that the bulb reservoir is here replaced by a two-neck Wolff bottle with a tubulure at the bottom, and an iron tube containing metallic calcium is used in place of a glass tube filled with magnesium turnings. A small Wolff bottle, *A*, that has two necks and a tubulure at

¹ *Berichte der deutschen chemischen Gesellschaft*, 41 (1908), 2017.

² *Experimental Study of Gases*, 101.

³ *J. Chem. Soc.*, 55 (1889), 110.

the bottom is connected with the level-bulb *B* by means of enamelled rubber tubing. Into the two necks of the Wolff bottle are inserted, by means of rubber stoppers, two glass tubes, one with a two-way stopcock and the other with a single stopcock. The tube *D* is bent as shown in the figure and is provided with a small bulb *S* for catching any mercury that may be carried up

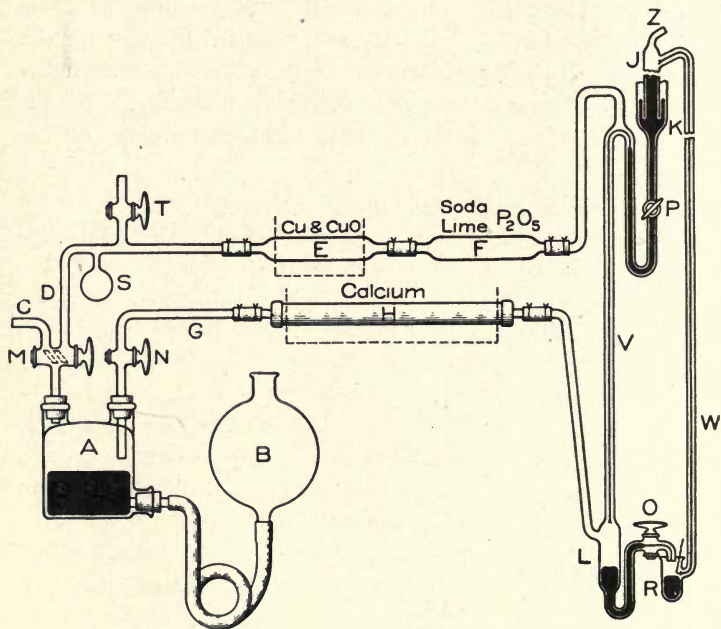


FIG. 82

through *D*. The apparatus may be connected with a mercury air pump through the side-arm *T*. The end of *D* is connected by rubber tubing, securely wired in place, with the tube *E* of Jena glass containing partially reduced copper oxide, and the tube *F* containing soda lime and phosphorus pentoxide. The tube *G* is connected with the tube *H* which is of iron, and is about 1.5 meter long and about 2 cm. inner diameter. *H* is filled

with pieces of metallic calcium, or, if this not available, with the mixture of magnesium, freshly ignited lime and metallic sodium recommended by Hempel. **E* and *H* rest in combustion furnaces. The metallic copper is used for the removal of any oxygen that might be present in the gas mixture. The copper oxide serves to oxidize hydrogen and carbon monoxide. Hydrogen may result from the action of water vapor upon the metallic calcium. The carbon monoxide may diffuse into the apparatus through the hot iron tube. To avoid this last mentioned difficulty Franz Fischer and Hähnel¹ suggest that the iron tube be surrounded by sheet copper 2 mm. thick.

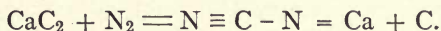
The further ends of *F* and *H* are connected with the Collie apparatus in the manner shown in the figure. To prepare the apparatus for use the level-bulb *B* is raised and mercury is forced up to the stopcock *N* and through the stopcock *M* to the end of the branch tube *C*, and *M* and *N* are then closed. *C* is now connected with the gasometer containing the gas mixture to be treated, *M* is opened, *B* is lowered and the gas is drawn into the bottle *A*. *M* is then closed. The stopcocks *O* and *P* are also closed, the tubes *F* and *H* are heated and the apparatus is exhausted through *T* by means of a mercury pump until gases cease to be given off. *T* is then closed and *M* is carefully turned to such a position that *A* communicates with *D*, *N* is next opened and then the stopcock *P*. Mercury from the reservoir *K* now drops down through the capillary tube *V* carrying with it gas into *L* and forcing the gas through *H*. The stopcock *O* is turned so that mercury flows from *L* into *R* in a steady stream. *R* is provided with a side capillary tube *W* which connects with the tube *J*, this latter tube dipping into the mercury in the reservoir *K*. The upper end of the tube *J* is connected through *Z* with a water suction pump. A twisted piece of rusty iron wire is inserted in the lower end of the capillary tube *W* to prevent the mercury that flows into *R* from *L* from completely

¹ *Berichte der deutschen chemischen Gesellschaft*, 43 (1910), 1436.

closing the capillary. This results in the mercury being drawn up through *W* in a series of fine drops which fall into the reservoir *K*. In this manner the gases are continuously forced through *H* and *A* and back through *D*, *E* and *F*, and the process will run for hours without attention if the iron wire was properly adjusted and the flow of mercury was carefully regulated at the beginning of the experiment.

Further amounts of the original gas mixture may be introduced through *C* when desired. After all of the gases except those of the argon group have been removed, the gas mixture remaining in the apparatus may be pumped out through *T* by means of a Töpler pump, and collected as described on page 13, or the stopcock *N* may be closed, and such of the gas residue as is in *A* may be driven out through *C* into a suitable container by raising the level-bulb *B* and turning the stopcock *M* into the proper position.

For the removal of large amounts of nitrogen from the air Franz Fischer and Ringe¹ have employed commercial calcium carbide. This substance reacts at high temperatures with nitrogen with the formation of calcium cyanamide and the separation of carbon, according to the equation,



They find that this reaction does not reverse at a temperature of about 800°, and that both nitrogen and oxygen may quantitatively be removed by this means. The calcium carbide is placed in a thick-walled iron cylinder of sufficient size to hold about seven kilograms of the carbide. The operation is conducted in a manner essentially similar to that already here described, except that the circulating device differs from that employed by Collie and Travers.

¹ *Berichte der deutschen chemischen Gesellschaft*, 41 (1908), 2017.

GASES OF THE ARGON GROUP

	Density	Absolute melting point	Absolute boiling point at 760 mm.	Critical temperature	Critical pressure in atmospheres	Per cent by weight in air
Helium . . .	1.98		4.5	5°	2.3	0.000056
Neon . . .	9.97	20	30	53°	29.	0.00086
Argon . . .	19.95	83.4	87	156°	52.9	1.3
Krypton . . .	41.5	104	121	211°	54.3	0.028
Xenon . . .	65.35	133	164	288°	57.2	0.005

 NITROUS OXIDE (N₂O)

Properties of Nitrous Oxide. — Specific gravity, 1.5229; weight of one liter, 1.9688 grams.

Nitrous oxide is quite soluble in water. One volume of water dissolves, at 760 mm. pressure and 20°, 0.670 volume (Carius).

The coefficient of absorption is —

$$1.30521 - 0.045362t + 0.0006843t^2.$$

For alcohol it is —

$$4.17805 - 0.069816t + 0.000609t^2,$$

and 1 volume of alcohol takes up at 20° 3.0253 volumes N₂O.

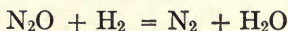
Detection of Nitrous Oxide. — No satisfactory method has yet been devised for the detection of small amounts of nitrous oxide. Lunge has proposed ¹ that the gas mixture under examination be passed through absolute alcohol in which nitrous oxide is quite readily soluble while the other gases with which it is usually associated are not appreciably dissolved. The method serves merely to concentrate the nitrous oxide and cannot be regarded as a means of its identification.

¹ *Berichte der deutschen chemischen Gesellschaft*, 14 (1881), 2188.

The procedure suggested by Hempel¹ is similar in character, the gases being condensed by means of liquid air and then fractionally distilled. This yields a residue rich in nitrous oxide, in which the presence of the gas is indicated by the increase in volume that results when it is dissociated by mixing with it oxyhydrogen gas and exploding the mixture.

Determination of Nitrous Oxide. — For the determination of nitrous oxide a variety of methods has been proposed. Wagner² passes the gas over a hot mixture of chromium oxide and sodium carbonate. The nitrous oxide is reduced to nitrogen, while any nitric oxide that may be present is unaffected. The amount of nitrous oxide may be calculated from the volume of nitrogen set free, or from the amount of sodium chromate that is formed.

Von Dumreicher³ burns the gas with hydrogen in a eudiometer. Water and nitrogen are formed, and the latter is measured. Hempel recommends⁴ this method but adds oxyhydrogen gas also. He uses his explosion pipette for the combustion and finds that the results are satisfactory if the volume of hydrogen is two to three times that of the nitrous oxide and if, further, such an amount of oxyhydrogen gas is added as will give 26 to 64 volumes of combustible gas to every 100 volumes of incombustible gas. The decrease in volume is equal to the volume of nitrous oxide.



Von Knorre and Arndt⁵ pass a mixture of nitrous oxide and hydrogen through a hot Drehschmidt capillary tube (see p. 154) and obtain satisfactory results. They also find that this method gives approximately accurate results in the analysis of a mix-

¹ *Zeitschrift für Elektrochemie*, **12** (1906), 600.

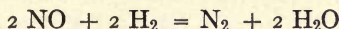
² *Zeitschrift für analytische Chemie*, **21** (1882), 374.

³ *Kais. Akad. d. Wissen. Wien*, **82** (1881), 560.

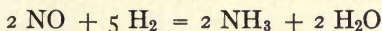
⁴ *Berichte der deutschen chemischen Gesellschaft*, **15** (1882), 903. See also *Zeit. für Elektrochemie*, **12** (1906), 600.

⁵ *Berichte der deutschen chemischen Gesellschaft*, **32** (1899), 2136; **33** (1900), 30.

ture of nitrous oxide and nitric oxide. An excess of hydrogen is added to the gas mixture and the gases are then *slowly* passed through a Drehschmidt capillary tube heated to bright redness.



Too rapid passage of the gas will cause the formation of some ammonia from the nitric oxide.



The volumes of the two oxides of nitrogen in the gas mixture may be calculated from the contraction. If V = the volume of the gas mixture, and C = the contraction, then

$$\begin{aligned} V &= \text{vol. N}_2\text{O} + \text{vol. NO}, \\ C &= \text{vol. N}_2\text{O} + 1\frac{1}{2} \text{ vol. NO}, \end{aligned}$$

and from the foregoing

$$\text{vol. NO} = 2 (C - V).$$

If nitrogen also is present, then

$$\begin{aligned} V &= \text{vol. N}_2\text{O} + \text{vol. NO} + \text{vol. N}_2 \\ C &= \text{vol. N}_2\text{O} + 1\frac{1}{2} \text{ vol. NO} \\ \text{vol. H}_2 &= \text{vol. N}_2\text{O} + \text{vol. NO}, \end{aligned}$$

from which it follows that

$$\begin{aligned} \text{vol. N}_2\text{O} &= 3 \text{ vol. H}_2 - 2 C \\ \text{vol. NO} &= 2 (C - \text{vol. H}_2) \\ \text{vol. N}_2 &= V - \text{vol. H}_2. \end{aligned}$$

Baskerville and Stevenson ¹ determine nitrous oxide by passing the gas over hot copper, reducing the copper oxide by hydrogen, and collecting and weighing the water that is formed. They carry out the method as follows: The hydrogen is generated in a Kipp apparatus from zinc and sulphuric acid (1:6) to which

¹ *Jour. Ind. and Eng. Chem.*, 3 (1911), 579.

two drops of chloroplatinic acid have been added. The gas is passed through solid sodium hydroxide and a long tube filled with calcium chloride to remove acid gases and moisture. The calcium chloride tube is connected to a combustion tube of hard glass that is 100 cm. long and is filled for 70 cm. of its length with snugly fitting rolls of copper gauze. The further end of the combustion tube is drawn out to fairly small diameter, and the end is inserted into a tube filled with calcium chloride, the joint between the two being made air tight with a piece of rubber tubing. A second tube filled with calcium chloride is joined to the first and to the further end of this tube there is connected a delivery tube that dips into water or some other liquid in a test tube and serves to show the speed of flow of the gas. The combustion tube rests upon an iron trough in a combustion furnace.

Hydrogen is now passed through the combustion tube until most of the air has been expelled. The tube is then heated to dull redness and the passage of hydrogen is continued until the copper is completely reduced. The tubes containing calcium chloride are weighed and are now connected to the combustion tube in the manner above described. The hydrogen is then discontinued and about 800 cc. of the gas sample is passed into the tube that contains sodium hydroxide and through the rest of the apparatus, the speed of flow of the gas being about two bubbles per second. The volume of the gas sample and its temperature and pressure are noted before the gas is passed through the apparatus. To insure complete decomposition of the nitrous oxide by the hot copper the operation should be so conducted that the last 15 cm. of copper gauze undergoes no oxidation. After the sample of gas has been passed through the chain, hydrogen is again admitted to the apparatus and is passed through it at the rate of from three to four bubbles per second until the copper oxide that has been formed is entirely reduced, and the water is completely driven out of the tube and into the weighed tubes containing calcium chloride. The operation is then presumably completed, although the authors give no

further details, by discontinuing the heating of the combustion tube and, when the apparatus is cold, passing dry air through the calcium chloride tubes until the hydrogen with which they are filled is displaced. They are then weighed and the amount of nitrous oxide in the gas sample is calculated from the weight of water that has been formed.

The method cannot be used for the determination of nitrous oxide in gas mixtures that contain other oxides of nitrogen or oxygen or other gases that would be decomposed by the metallic copper with the formation of copper oxide, unless the amounts of these gases are determined and the water that results from them is subtracted from the total amount of water found. Baskerville and Stevenson find that these gases are not present in the samples of commercial compressed nitrous oxide that they analyzed.

NITRIC OXIDE (NO)

Properties of Nitric Oxide.—Specific gravity, 1.0378; weight of one liter, 1.3417 grams.

Nitric oxide is but slightly soluble in water, one volume of water dissolving only about $\frac{1}{20}$ volume of the gas. It is more soluble in alcohol, the coefficient of absorption for temperatures between 0° and 25° being, according to Carius,

$$0.31606 - 0.003487 t + 0.000049 t^2.$$

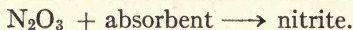
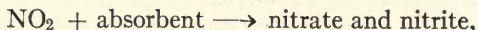
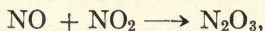
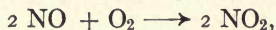
Nitric oxide cannot be kept over water without undergoing change. Nitrous acid is formed together with some hyponitrous acid which breaks down partly into nitrous oxide and partly into ammonia. The latter then reacts with the nitrous acid and liberates nitrogen, which accounts for the presence of this gas in quite large amount in nitric oxide that has been stored over water for a considerable length of time.

Nitric oxide is absorbed by solutions of ferrous salts, potassium permanganate, potassium dichromate, and alkaline sodium sulphite. It is also taken up by concentrated sulphuric acid,

one cc. of this acid of 1.84 specific gravity absorbing 0.035 cc. of nitric oxide. If the acid has a specific gravity of 1.5, one cc. of it will absorb 0.017 cc. of the gas.

Hydrogen dioxide reacts with nitric oxide to form nitric acid and water.

Detection of Nitric Oxide. — A delicate method for the detection of nitric oxide consists in passing the gas, mixed with air, through a dilute solution of the hydroxide of either sodium or potassium and adding Griess's reagent. The reactions that take place in the absorption are, according to Le Blanc,¹ as follows:



The nitrite that has thus been formed in the absorbent is detected by first adding acetic acid to the sodium hydroxide or potassium hydroxide until the solution has a faint acid reaction and then adding Griess's reagent as improved by Ilosvay² and Lunge.³ The reagent in this modified form is prepared as follows: 0.5 gram of sulphanilic acid is dissolved in 150 cc. of dilute acetic acid. 0.1 gram of solid α -naphthylamine is boiled with 20 cc. of water, the colorless solution is poured off from the violet residue and to the solution 150 cc. of dilute acetic acid is added. The two solutions are then mixed and the reagent is kept in a tightly stoppered bottle.

Lunge states that the reagent is not at all affected by the light. This is contradicted by Reckleben, Lockemann and Eckardt⁴ who state that even in diffused daylight the reagent soon takes on a yellowish-red color which renders the detection of small amounts of nitrous acid impossible. They find that if

¹ *Zeit. für Elektrochemie*, 12 (1906), 541.

² *Bull. soc. chim.* (3), 2 (1889), 347.

³ *Z. f. angew. Chem.*, 1889, 666.

⁴ *Z. f. analyt. Chem.*, 46 (1907), 671.

the solution is kept in the dark it remains completely clear and colorless for months.

In making the test the acidified solution of the absorbent is warmed to about 80° and about one-fifth of its volume of the Griess's reagent is added. If nitric oxide was present in the gas mixture, the solution turns red. The reaction is extremely delicate, one part of nitrous acid in one thousand million parts of the solution giving a distinct red coloration after one minute.

Determination of Nitric Oxide. — Nitric oxide may quantitatively be determined by absorption of the gas with a solution of ferrous sulphate. The reagent contains one part by weight of the salt dissolved in two parts by weight of water, and it is very slightly acidified with dilute sulphuric acid. It is used in a Hempel double pipette for liquid reagents. The analytical absorbing power of this solution is 2.5. This reagent, however, tends to give up the absorbed nitric oxide to indifferent gases, and the method does not yield correct results when nitrous oxide is present with the nitric oxide.

It has been proposed to determine nitric oxide by mixing it with hydrogen and burning the mixture in a Drehschmidt capillary tube (see under Nitrous Oxide). Moser, who has recently made a careful comparison of the various methods for the determination of this gas states¹ that this method does not yield uniform results both because of the secondary reaction which causes the formation of ammonia and because of the porosity of red-hot platinum to gases.

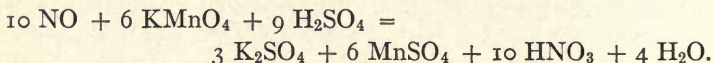
The absorption of nitric oxide by sodium sulphite is original with Divers,² who, however, gives no details concerning the preparation of this solution further than to say that it is "a strong solution of either sodium or potassium sulphite to which a little alkali hydroxide has been added." He states that it "quickly absorbs every trace of nitric oxide, which it fixes in the form of hyponitrososulphate, $\text{Na}_2\text{N}_2\text{O}_2\text{SO}_3$."

¹ *Z. f. analyt. Chem.*, 50 (1911), 401.

² *Jour. Chem. Soc.*, 75 (1899), 82.

Moser finds that this reagent is not superior to ferrous sulphate and that the absorption by sodium sulphite takes place quite slowly and is complete only after long shaking.

A satisfactory titrimetric method for the determination of nitric oxide is that based upon the reaction between the gas and an acidulated solution of potassium permanganate.



The reaction was first examined by Terreil¹ who found that nitric oxide is completely oxidized to nitric acid by a neutral or an acidified solution of potassium permanganate, while nitrous oxide is not attacked. Lunge² ascertained that the speed of reaction between nitric oxide and a $\frac{\text{N}}{10}$ solution of potassium permanganate is so slight that complete absorption of the gas is attained only when an apparatus that brings about prolonged and intimate contact between the gas and absorbent is employed. He recommends for this purpose the ten-bulb tube shown on page 359, but better results will undoubtedly follow the employment of a Friedrichs spiral gas washing bottle, page 123. Before beginning the determination the air in the apparatus must be displaced by carbon dioxide because of the reaction between nitric oxide and oxygen. To avoid this operation and also to obtain more complete absorption, Moser³ suggests that the gas mixture be passed into a spiral absorption bulb that is made entirely of glass and that is figured in his article. A simple and satisfactory substitute for this spiral bulb may be made by fusing to one of the tubes of the bulb of a Hempel gas pipette of about 130 cc. capacity a capillary tube about 3.5 cm. long, and to the other tube of the bulb a piece of glass tubing about 1 cm. external diameter and 20 cm. long. The bulb is placed in a clamp with the short capillary tube uppermost,

¹ *Comptes rendus*, 63 (1866), 970.

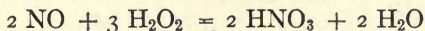
² *Z. f. angew. Chem.*, 1890, 567.

³ *Loc. cit.*

and the long stem is inserted into a wide mouth bottle of about 250 cc. capacity in which is placed a measured volume (about 200 cc.) of the standardized solution of potassium permanganate. The potassium permanganate is approximately decinormal in strength and to every 100 cc. of the solution is added from 30 to 50 cc. of 2 N sulphuric acid. The capillary tube of the bulb is closed by a short piece of rubber tubing and pinchcock. A water suction pump is connected to this tube, and the permanganate solution is drawn up until it fills the tube and reaches nearly to the top of the capillary tube. The gas burette containing the sample of gas under examination is connected with the bulb by means of the usual piece of bent capillary tubing and the gas sample is passed over into the bulb. The pinchcock at the top of the bulb is then closed and the bulb is disconnected from the burette. The bottle is grasped in the left hand and the lower tube of the bulb in the right hand, and with the end of the large tube of the bulb resting upon the bottom of the bottle, the bulb is shaken for about ten minutes to effect complete reaction between the nitric oxide and the potassium permanganate. The pinchcock at the top of the bulb is then opened and the solution is allowed to run out of the bulb down into the bottle, the bulb being finally rinsed with distilled water. An excess of a standardized solution of ferrous sulphate is added to the potassium permanganate and the excess of ferrous sulphate is titrated back with potassium permanganate.

The results by this method even when the Moser absorption bulb is employed are somewhat lower than those obtained by absorption with ferrous sulphate, which Moser ascribes to the reaction between the nitric oxide and the oxygen dissolved in the solution of potassium permanganate.

Schönbein¹ found that when nitric oxide was brought into contact with an excess of hydrogen dioxide the gas is oxidized to nitric acid:



¹ *J. f. prakt. Chem.*, 81 (1860), 265.

The applicability of this reaction to the determination of nitric oxide has been studied by Davis,¹ by Wilfarth² and by Lunge.³ Lunge discarded the method because his experiments indicated that the absorption of nitric oxide by hydrogen dioxide either in acid or in alkaline solution was not complete. Moser⁴ found that this criticism is correct when the method is carried out in the manner described by Wilfarth and by Lunge, but he states that with the absorption bulb that he devised it is possible to obtain complete oxidation of nitric oxide in from six to twelve minutes. He employs as absorbent a three per cent solution of hydrogen dioxide in a definite volume of which (about 110 cc.) the free acid is first determined by titration with a standardized solution of potassium hydroxide, using a one per cent solution of phenolphthalein as indicator. The reagent is then brought into the absorption bulb, the gas is passed in from a gas burette, and the gas and hydrogen dioxide are shaken together for several minutes. The absorbent is then transferred to a beaker and the nitric acid that has been formed is titrated with potassium hydroxide. If acid or alkaline gases are present in the gas mixture under examination they must first be removed by passing the mixture through suitable absorption apparatus. Under such conditions, however, the determination of the nitric oxide with potassium permanganate is preferable to that with hydrogen dioxide.

Determination of Nitrites in the Atmosphere.—The method of Ilosvay and Lunge for the detection of nitrites may also be employed for the determination of nitrites in the atmosphere. A measured amount of air is drawn through a solution of sodium hydroxide or potassium hydroxide and the color that results when Griess's reagent is added under the conditions above prescribed is compared with the color yielded by a standard nitrite solution. For approximate work the standard solution

¹ *Chemical News*, 41 (1880), 188.

² *Z. f. analyt. Chem.*, 23 (1884), 587.

³ *Z. f. angew. Chem.*, 1890, 568.

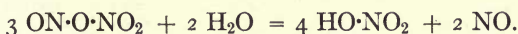
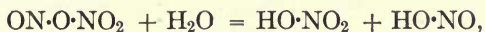
⁴ *Loc. cit.*

may be prepared by dissolving a weighed amount of either potassium nitrite or sodium nitrite in water. If greater accuracy is desired the standard nitrite solution may be prepared by precipitating a solution of silver nitrate with sodium nitrite, recrystallizing the silver nitrite twice from hot water and then adding to its solution in hot water sodium chloride, and removing the precipitated silver chloride by filtration.

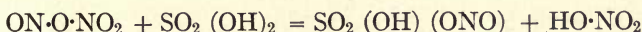
NITROGEN TETROXIDE (N_2O_4)

Properties of Nitrogen Tetroxide.— Specific gravity (NO_2), 1.5906. Weight of one liter (NO_2), 2.0563 grams. The molecule of nitrogen tetroxide is considered to have the formula N_2O_4 at temperatures below -11° and to dissociate into NO_2 as the temperature rises. At the average temperature of the laboratory the gas will contain both the simpler molecule NO_2 and the polymer N_2O_4 .

When brought into contact with water, nitrogen tetroxide forms nitric acid, nitrous acid and nitric oxide, according to the equations



When nitrogen tetroxide is passed through a dilute solution of sodium hydroxide, oxygen or air being absent, sodium nitrite and nitrate are formed¹ in the proportions shown in the first equation above. If, however, oxygen or atmospheric air is present with the nitrogen tetroxide, some of the nitrite is oxidized to nitrate. The gas is rapidly absorbed by concentrated sulphuric acid (1.7 to 1.8 sp. gr.). nitrosyl sulphuric acid and nitric acid being formed.



¹ Lunge and Berl, *Z. f. angewandte Chem.*, 19 (1906), 857.

Nitrogen tetroxide may be detected by absorbing the gas in a dilute solution of sodium hydroxide, acidifying this with acetic acid and adding Griess's reagent. (See under Nitric Oxide.)

AMMONIA (NH_3)

Properties of Ammonia. — Specific gravity, 0.5895; weight of one liter, 0.7621 gram. One gram of water absorbs, at a pressure of 760 mm.,

at	0°, 0.875 gram	(1129 cc.)
"	10°, 0.679	" (876 ")
"	20°, 0.526	" (678 ")

Alcohol and ether also absorb considerable quantities of the gas.

Detection of Ammonia. — Ammonia may be detected when present in fairly large amounts by means of litmus paper or turmeric paper. A more sensitive reagent for the detection of minute amounts of ammonia is Nessler's reagent which is an alkaline solution of potassium mercuric iodide, K_2HgI_4 . When ammonia acts upon this solution mercurammonium iodide



is formed. If the amount of ammonia is appreciable, the compound appears as a reddish brown precipitate. With smaller amounts of ammonia it imparts merely a yellow color to the solution. The reaction is very delicate; 0.05 mg. of ammonia in one liter of water can readily be detected.

Determination of Ammonia. — Ammonia may be determined by passing the gas mixture through a measured amount of dilute hydrochloric or sulphuric acid of known strength and titrating the excess of acid with a standard solution of an alkali, using litmus or methyl orange as indicator.

If the amount of ammonia in the gas mixture is very small, as for example in atmospheric air, the ammonia may be absorbed by passing it through ammonia-free distilled water slightly acidified with sulphuric acid and then determining the ammonia colorimetrically with Nessler's reagent.

CARBON DIOXIDE (CO_2)

Properties of Carbon Dioxide. — Specific gravity, 1.5201; weight of one liter, 1.9652 grams.

According to Naccari and Pagliani one volume of water absorbs, between 17° and 27° ,

$$1.5062 - 0.036511 t + 0.0002917 t^2.$$

One cc. of sulphuric acid (sp. gr. = 1.78) dissolves, at 14°C . and 816.4 mm. pressure, 1.16 cc. of carbon dioxide.

Carbon dioxide is readily absorbed by a solution of potassium hydroxide or of barium hydroxide.

Determination of Carbon Dioxide. — For the volumetric determination of the gas, a solution of one part of caustic potash in two parts of water is employed. The analytical absorbing power of this solution is 40. For the rapid and approximate determination of carbon dioxide by means of this absorbent, the Honigmann gas burette (page 72) may be used. With the Bunte gas burette (page 74) somewhat more accurate results can be obtained.

The most satisfactory forms of absorbing apparatus for use in technical gas analysis are the spiral pipette described on p. 81 or the Hempel simple pipette for solid and liquid reagents (Fig. 35). With the latter the cylindrical part *C* is first closely filled with very short rolls of iron wire gauze. The gauze has a mesh of 1 to 2 mm., and the rolls are from 1 to 2 cm. long and about 5 mm. thick. The high viscosity of the reagent causes it to cling to the wire gauze when the gas is passed into the pipette and, as a consequence, the absorption of the carbon

dioxide is very rapid. The viscosity of the reagent serves also to protect the iron wire gauze from oxidation by any oxygen in the gas mixture. Unless the amount of carbon dioxide in a gas mixture is unusually high, it is quantitatively removed by simply passing the gas once into either pipette and allowing it to remain there a few seconds.

Special methods for the determination of small percentages of carbon dioxide such as are found, for example, in atmospheric air are described in Chapter XVIII.

CARBON MONOXIDE (CO)

Properties of Carbon Monoxide. — Specific gravity, 0.9673; weight of one liter, 1.2506 grams. One volume of water dissolves, according to L. W. Winkler,

at	0°	0.03537	vol. of CO
"	10°	0.02816	" "
"	20°	0.02319	" "

According to Carius, alcohol dissolves, between 0° and 25°, 0.20443 volume of carbon monoxide.

Detection of Carbon Monoxide by Blood Spectrum. — The most delicate and dependable method for the detection of carbon monoxide is that in which the gas is absorbed by a solution of blood and the resulting carbon monoxide hæmoglobin is detected by the spectroscope. When a dilute solution of pure blood is brought before the slit of the spectroscope, two absorption bands, lying between the Fraunhofer lines *D* and *E*, are seen (Fig. 83, spectra No. 1 and No. 2). If, now, a reducing agent, such as ammonium sulphide, is added to the blood solution, these two bands, which are due to the oxyhæmoglobin of the blood, disappear and are replaced by a single broad and weakly defined band (spectrum No. 4).

When, however, carbon monoxide has previously been brought into contact with the blood solution, the two absorption

bands due to carbon monoxide hæmoglobin (spectrum No. 3) do not disappear when the reducing agent is added. Consequently the persistence of these two separate absorption bands is conclusive proof of the presence of carbon monoxide in the gas mixture under examination.

The solution of blood for use in this test is prepared by freeing a sample of blood from fibrin by beating it with a bundle of straws and then diluting the clear blood with an equal volume of a cold, saturated solution of borax. The addition of borax

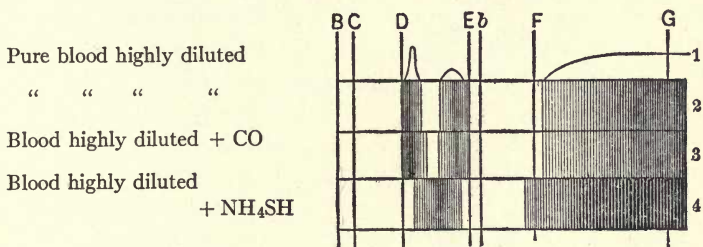


FIG. 83

prevents putrefaction and does not change the spectroscopic properties of the blood, reduction and combination with oxygen and carbon monoxide taking place just as readily as if fresh blood or a solution of hæmoglobin were employed. The solution used in the absorption of carbon monoxide is prepared from the concentrated solution by mixing one cc. of the latter with 19 cc. of water. This gives a blood solution of the concentration 1 in 40. The absorption of carbon monoxide by this dilute blood solution may be effected by filling a 100 cc. bottle with water, emptying it in the room of which the air is to be tested for carbon monoxide, introducing 3 cc. of the dilute blood solution into the bottle, inserting the stopper in the bottle and then thoroughly shaking the bottle to bring the blood into contact with the inclosed gas. A more efficient absorption apparatus is that designed by Wolff¹ (Fig. 84). In preparing this

¹ *Correspondenzblatt des Vereins analytischer Chemiker*, 3 (1880), 46.

apparatus for use a small wad of glass wool is inserted into *d* from above and gently pressed into place. The tube is then filled up to *f* with moderately fine, powdered glass. The grains of glass should be about as large as those of ordinary gunpowder and before its introduction into the tube the glass should be thoroughly cleaned by boiling it with hydrochloric acid, and washing it with distilled water. Two cc. of the dilute blood solution (1 in 40) is then introduced through *a* from a pipette.

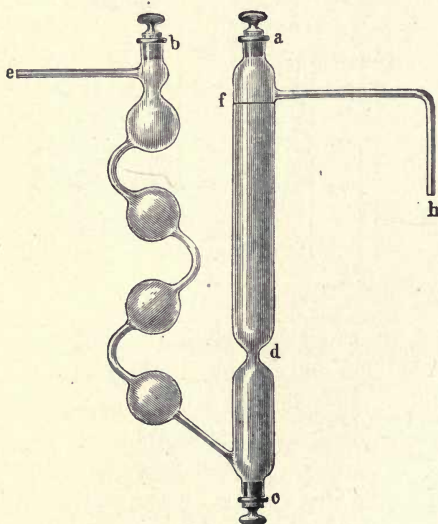


FIG. 84

a is closed and by gently blowing into *h* the blood solution is caused to uniformly distribute itself throughout the column of powdered glass. The side tube *e* is now connected with the gas mixture (air) that is to be tested for carbon monoxide, and the gas is driven or drawn through the absorption tube, its volume being measured by a gas meter or other suitable device attached to *h*. To prevent the evaporation of

the water from the blood solution in the absorption apparatus, it is advisable to insert between *e* and the source of gas a U-tube or wash bottle containing sufficient water to keep the entering air saturated with moisture. If only very small amounts of carbon monoxide are to be expected, a sample of air of about 10 liters should be passed through the absorption apparatus at a rate of about 3 liters per hour. If it is not convenient to set up the apparatus in or near the room whose atmosphere

is to be tested, the sample may be collected in a 10 liter bottle by filling the bottle with water and emptying it in the room.

After the absorption of carbon monoxide by the blood solution has been accomplished in either of the two ways above described, it is transferred to a small test tube and examined with a spectroscope. If the Wolff absorption tube has been used, the blood solution is removed after the test by taking out the stoppers *a* and *c*, placing the test tube under *c*, and slowly dropping pure water upon the powdered glass. The liquid is collected in the test tube until the volume amounts to 3 cc. Since 2 cc. of the dilute blood solution (1 in 40) was originally used, the resulting 3 cc. of solution would now have a concentration of 1 in 60.

Any spectroscope of not too great dispersion may of course be employed for the examination of the blood spectrum, but a small direct vision spectroscope is quite as satisfactory for this purpose as a larger one. For checking the result of the spectroscopic examination a second small test tube should be filled with the original blood solution, also diluted to 1 in 60, that has not been exposed to the action of the gas. One drop of a strong solution of ammonium sulphide is added to the contents of each tube, the tubes are corked and thoroughly shaken, and the spectra are examined after the tubes have stood for about half an hour. The presence of the two absorption bands shown in Fig. 83, spectrum No. 3, in the blood solution that has been exposed to the gas, and the absence of these bands in the solution of pure blood is conclusive proof of the presence of carbon monoxide in the air under examination. When the test is made in this manner the delicacy of the method is about 0.03 per cent by volume of carbon monoxide.

Kostin has found ¹ that if the oxygen of the air is first removed, the delicacy of the blood test for carbon monoxide is greatly enhanced, and that under these conditions one part of the gas in forty thousand parts of air may be detected. The removal of

¹ *Archiv für die Gesamte Physiologie*, 83 (1901), 572.

oxygen may be effected by passing the air through 3 liters of a saturated solution of ferrous sulphate to which 1 liter of strong ammonium hydroxide has been added. The solution is placed in an aspirator bottle that is filled with iron wire gauze (A, Fig. 85). Four liters of this solution which contains much undissolved ferrous hydroxide is able to absorb the oxygen contained in 80 liters of air. Two such bottles are employed, the air under examination being first drawn into one and then

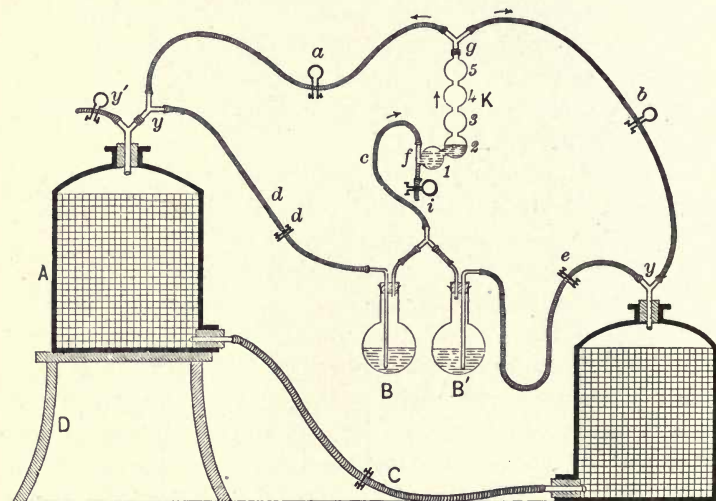


FIG. 85

driven into over the other, and passed backwards and forwards between the two aspirators until all oxygen has been removed. The residual gas is next forced from one aspirator into the other through one of the washing flasks *BB'* and the absorption apparatus *K* containing the blood solution. The washing flasks are charged with oxalic acid for the removal of any ammonia that may be given off from the material in the aspirator bottles.

Ogier and Kohn-Abrest remove ¹ oxygen by means of a solu-

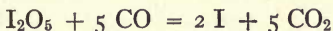
¹ *Ann. chim. analyt. appl.*, 13 (1908), 218.

tion of sodium hyposulphite, which is probably more rapid in its action and more convenient to handle than is the reagent used by Kostin.

Some investigators are of the opinion that the best method for detecting the presence of carbon monoxide in blood is that suggested by Kunkel. The blood is here diluted with 10 volumes of water and an equal volume of a 3 per cent tannin solution is then added. If the blood contains carbon monoxide, a reddish precipitate is formed, while with normal blood the precipitate is dark brown. These color reactions become especially distinct after five or six hours.

On the other hand, Doepner¹ states that the spectroscopic detection of carbon monoxide in blood is fully as satisfactory as the best of the precipitation methods.

Detection of Carbon Monoxide by means of Iodine Pentoxide.—Iodine pentoxide and carbon monoxide react on each other with the liberation of free iodine and the formation of carbon dioxide.



C. de la Harpe and Reverdine² first utilized this reaction for the detection of carbon monoxide. More recently Levy and Pecoul³ find that by passing the liberated iodine into chloroform, minute amounts of carbon monoxide in air can be detected. They state that one volume of carbon monoxide in 10,000 volumes of air will set free sufficient iodine to give to the chloroform an intense color. If acetylene is present in no greater proportion than 1:10,000, it will cause no coloration of the chloroform, but larger amounts of acetylene should be removed before the test is made.

Determination of Carbon Monoxide by Absorption.—For the absorption and volumetric determination of carbon monoxide a hydrochloric acid or an ammoniacal solution of cuprous chloride is employed.

¹ *Z. f. Medizinalbeamte*, 22 (1909), 287.

² *Chem. Ztg.* 12 (1888), 1726.

³ *Comptes rendus*, 142 (1906), 162.

The hydrochloric acid solution of cuprous chloride may be prepared, according to Winkler, by adding a mixture of 86 grams of copper oxide and 17 grams of finely divided metallic copper to 1086 grams of hydrochloric acid (sp. gr. = 1.124), the mixture being slowly introduced and the acid frequently stirred. The copper powder is best prepared by the reduction of copper oxide with hydrogen. After this mixture has been added to the acid, a spiral of copper wire reaching from the bottom of the bottle up to its neck is inserted, and the bottle is closed with a soft rubber stopper. The solution is dark in the beginning, but upon standing it becomes wholly colorless. In contact with the air, however, it again turns dark brown, and some cupric chloride forms.

The analytical absorbing power of the solution is 4 cc. of carbon monoxide.

Another method somewhat more rapid and convenient than that just described is given by Sandmeyer.¹

Twenty-five parts of crystallized copper sulphate and 12 parts of dry sodium chloride are placed in 50 parts of water and heated until the copper sulphate dissolves. Some sodium sulphate may separate out at this point, but the preparation is continued without the removal of this salt. 100 parts of concentrated hydrochloric acid and 13 parts of copper turnings are then added and the whole is boiled in a flask until decolorized. To avoid excessive evaporation it is desirable to insert in the neck of the flask a tall condensing tube or an upright condenser. The addition of platinum foil to the contents of the flask will facilitate reduction. The solution should be kept in bottles that are filled up to the neck and are closed by rubber stoppers.

The ammoniacal solution of cuprous chloride may be prepared as follows: —

800 cc. of the hydrochloric acid solution prepared by the Winkler method given above or 1200 cc. of the Sandmeyer solution is poured into about 4 liters of water, and the resulting

¹ *Berichte der deutschen chemischen Gesellschaft*, 17 (1884), 1633.

precipitate is transferred to a graduated stoppered cylinder of 250 cc. capacity. After about two hours the precipitate and liquid which is above the 50 cc. mark is drawn off by means of a siphon and 7.5 per cent ammonium hydroxide is added up to the 250 cc. mark. The stopper is inserted, the cylinder is well shaken, and it is then allowed to stand for several hours. A solution prepared in this manner has so slight a tension that the latter may in nearly every case be disregarded.

The analytical absorbing power of this solution is 6 cc. of carbon monoxide.

Frischer suggests ¹ the preparation of an ammoniacal solution of a cuprous salt by adding ferrous sulphate to an ammoniacal solution of cupric sulphate, but he gives no specific directions.

Solutions of cuprous chloride have no considerable tension, so that this may be disregarded in analyses in which only approximate results are desired. In very exact determinations, however, the gases that have been in contact with the reagent must be freed from hydrogen chloride or from ammonia.

The solutions of cuprous chloride may conveniently be used in the Hempel double pipettes for liquid reagents (Fig. 36).

If, after the absorption of carbon monoxide in a gas mixture, the hydrogen is to be determined with palladium, the ammoniacal solution must be used. If the amount of carbon monoxide alone is to be ascertained, the hydrochloric acid solution may be employed with equally good results.

H. Drehschmidt ² has shown, however, that the union of carbon monoxide with cuprous chloride is so feeble that upon shaking a solution that has taken up any considerable quantity of carbon monoxide, this gas is again given up in an atmosphere free from carbon monoxide. For this reason two pipettes are used in the absorption, one pipette containing a solution of cuprous chloride that has been in use some time, the other a solution

¹ *Chem. Ztg.*, **32** (1908), 1005.

² *Berichte der deutschen chemischen Gesellschaft*, **20** (1887), 2344, 2752; and **21** (1888), 2158.

that has been but little used. In the absorption, the gas in question is first shaken for two minutes with the first-mentioned solution, is drawn back into the burette and is then passed into the second pipette containing the but slightly used solution, and is shaken three minutes therein. According to Drehschmidt, the ammoniacal solution is to be preferred to the hydrochloric acid one.

The results obtained by Gautier and Clausmann¹ in their experiments on the removal of carbon monoxide by absorption with cuprous chloride demonstrate the necessity of using two solutions of cuprous chloride as Drehschmidt recommends, and of *shaking* the gas with the absorbent, and furnish convincing evidence of the difficulty of effecting complete removal of carbon monoxide in the apparatus of Elliott or with the form of absorption pipette customarily employed in the Orsat apparatus. Producer gas contains a high percentage of carbon monoxide (sometimes as high as thirty per cent) and a comparatively small amount of hydrogen. In the analysis of such gas mixtures it should be borne in mind that the analytical absorbing power of the acid solution of cuprous chloride is only 4, and of the ammoniacal solution of cuprous chloride only 6, and that the absorption of carbon monoxide by either of these reagents becomes quite slow even before these limits are reached. It is consequently of particular importance that record be kept of the volume of carbon monoxide that the absorbent has taken up, and that the absorbent be renewed as soon as it has lost its efficiency.

Certain gases other than carbon monoxide are soluble to an appreciable degree in solutions of cuprous chloride. This renders it necessary, if accurate results are to be obtained, to saturate the cuprous chloride solution with those gases that are slightly soluble in it before proceeding to the absorption of carbon monoxide.

Solutions of cuprous chloride absorb not only carbon mon-

¹ *Compt. rend.*, 142 (1906), 485.

oxide, oxygen and acetylene, but also the so-called heavy hydrocarbons. For this reason the heavy hydrocarbons, even if their determination is not desired, must be removed from the gas mixture before the carbon monoxide is absorbed by cuprous chloride. Failure to do this is a frequent cause of erroneous results.

Determination of Carbon Monoxide by means of Iodine Pentoxide. — Nicloux¹ and Gautier² employ the reaction between iodine pentoxide and carbon monoxide (see p. 231) for the quantitative determination of the latter substance. Kinnicutt and Sanford³ have shown that this method can be used for the determination of very small amounts of carbon monoxide not only in air, but also in illuminating gas. The gas mixture under examination must first be freed from unsaturated hydrocarbons, hydrogen sulphide, sulphur dioxide, and similar reducing gases. To accomplish this Kinnicutt and Sanford pass the gas through two U-tubes, one containing sulphuric acid⁴ and the other small pieces of potassium hydroxide.⁵ The purified gas is then passed through a small U-tube containing 25 grams of iodine pentoxide. Inasmuch as this substance acts upon cork, rubber, and the usual lubricants, Morgan and McWhorter later suggested⁶ that the iodine pentoxide be placed in a U-tube with side arms, and that the large ends of the U-tube be then sealed before the blast lamp. The U-tube is suspended in an oil bath and its exit tube is joined to a Wolff absorption tube (see page 228) containing 0.5 grams of potassium iodide dissolved in 5 cc. of water. The oil bath is heated to 150° C. The temperature should not be allowed to rise much beyond 150° C., for Nowicki⁷ has found that iodine pentoxide itself begins to de-

¹ *Compt. rend.*, **126** (1898), 746.

² *Ibid.*, **126** (1898), 931.

³ *J. Am. Chem. Soc.*, **22** (1900), 14.

⁴ It would be preferable to place the sulphuric acid in a Friedrichs spiral gas washing bottle (see p. 123).

⁵ See also Weiskopf, *J. Chem. Met. Soc. S. Africa*, **9** (1909), 258, 306.

⁶ *J. Am. Chem. Soc.*, **29** (1907), 1589.

⁷ *Oesterr. Zeit. f. Berg-Hütt.*, **54** (1906), 6.

compose at 165° and is completely broken down at 300° . He also states that the oxidation of carbon monoxide by iodine pentoxide begins at 45° and is complete at 88° . From 250 cc. to 1000 cc. of the gas mixture under examination is then passed through the apparatus at the rate of about one liter in two hours. The iodine that is set free in the reaction is absorbed by the solution of potassium iodide in the Wolff tube.

Kinnicut and Sanford determined the amount of carbon monoxide in the gas mixture by titrating the free iodine with $N/1000$ solution of sodium thiosulphate; 0.002266 gram of iodine is equivalent to one cc. of carbon monoxide measured under standard conditions.

In the reaction between iodine pentoxide and carbon monoxide, one cc. of carbon monoxide yields one cc. of carbon dioxide which in the above method passes through the solution of potassium iodide. Morgan and McWhorter¹ recommend that as a check upon or substitute for the iodine titration, the liberated carbon dioxide be determined. This they do by passing the gas that issues from the Wolff tube through an absorption apparatus² containing 50 cc. of a solution of barium hydroxide such as is used in the Hesse method for the determination of carbon dioxide in air, and determining the volume of the absorbed carbon dioxide by titration with a standard solution of oxalic acid that contains 1.1265 grams of crystallized oxalic acid to the liter. Five cc. of this solution is equivalent to one cc. of carbon dioxide measured under standard conditions. Phenolphthalein, one part in 250 parts of alcohol, is used as indicator.

The above method for the determination of carbon monoxide by the use of iodine pentoxide gives very accurate results if the

¹ *Loc. cit.*

² They used a long test tube (24 x 2.5 cm.). This might advantageously be replaced by a glass cylinder about 20 cm. high and 4 cm. internal diameter, fitted with a three-hole rubber stopper carrying an inlet and exit tube, and the tip of a burette. Such an arrangement would permit of the titration of the solution of barium hydroxide without transferring it to another container and thus exposing it to the air.

carbon monoxide is present in quite small amounts. By means of it one part of carbon monoxide in 40,000 parts of air may be determined in as small an initial volume of air as one liter. It is, however, not suited to the determination of large amounts of carbon monoxide as Gill and Bartlett have shown ¹ in their examination of the method of Smits, Raken and Torwogt ² who had proposed the employment of the method for the determination of carbon monoxide in illuminating gas.

Colorimetric Determination of Carbon Monoxide. — Hal-dane has devised ³ a colorimetric method for the determination of small amounts of carbon monoxide in air. The method is based upon the fact that when oxygen and carbon monoxide are passed through a blood solution the amounts of oxyhæmoglobin and carbon monoxide hæmoglobin that are formed are in the ratio of the partial pressures of these two gases in the air, multiplied by a constant. The percentage of oxygen in the gas mixture can easily be determined by analysis, and if the value of the constant is known, the percentage of carbon monoxide in the gas can then be calculated from the relative amounts of oxyhæmoglobin and carbon monoxide hæmoglobin that are formed in a solution of blood through which the gas mixture in question has been passed.

A dilute solution of oxyhæmoglobin is of a yellow color, while that of carbon monoxide hæmoglobin is pink. The two solutions required for the colorimetric determination are — (1) A five per cent solution of defibrinated blood. This solution should be freshly prepared and should be kept in a stoppered bottle. (2) A solution of carmine, which is prepared by grinding one gram of carmine with a few drops of ammonium hydroxide in a mortar and dissolving the substance in 100 cc. of glycerine. Ten cc. of this liquid diluted to one liter with water forms the standard solution.

¹ *J. Ind. and Eng. Chem.*, 2 (1910), 9.

² *Z. f. angew. Chem.*, 1900, 1002.

³ *J. Physiol.*, 18 (1895), 461.

The air under examination is drawn through a bottle of about 200 cc. capacity fitted with a three-hole rubber stopper. In two of the openings of the stopper are inserted the inlet and outlet tubes for the passage of the air, and the third is closed by a glass plug. After the air originally in the bottle has been completely displaced by the air under examination, the rubber tubes attached to the glass tubes of the bottle are closed by pinch-cocks. The glass rod closing the third opening in the stopper is then removed, and there is inserted through this opening the tip of a small pipette that contains about five cc. of the blood solution. This solution is allowed to run down into the bottle, the pipette is withdrawn, the opening in the stopper is again closed with a plug, and the flask is gently shaken for about five minutes.

The blood solution is then transferred to a small colorimeter tube. In a second colorimeter tube of exactly the same dimensions, five cc. of the original blood solution is placed, and in a third tube five cc. of the blood solution that has been saturated with carbon monoxide by shaking the blood with coal gas. The standard carmine solution is now run from a burette into the second colorimeter tube until the color of the liquid is identical with that of the solution that has been saturated with carbon monoxide. The carmine solution is then added to the contents of the first test tube until the same tint is produced.

If x cc. of the carmine solution were run into a second tube, and y cc. into the first tube, then

$$\frac{y}{y + 5} \times \frac{x + 5}{x} \times 100 = S,$$

in which S is the percentage saturation of the blood that has been shaken with the air under examination. The amount of carbon monoxide in the air may then be calculated from the following table:

PERCENTAGE SATURATION	CARBON MONOXIDE IN AIR
10	0.015 per cent
20	0.04 "
30	0.08 "
40	0.12 "
50	0.16 "
60	0.22 "
70	0.30 "
80	0.60 "
90	1.2 "

The method is stated to give fairly accurate results for amounts of carbon monoxide in air between 0.015 and one per cent. With more than one per cent of carbon monoxide the gas should be diluted with air that is free from carbon monoxide.

Determination of Carbon Monoxide by Fractional Combustion. — Nesmjelow¹ has made an exhaustive study of the fractional combustion of carbon monoxide in the presence of hydrogen and methane. He summarizes the results of his experiments as follows:—

(1) That when hydrogen mixed with air is passed through a U-shaped tube that contains palladium asbestos and stands at the temperature of the room, the hydrogen is burned completely upon a single passage of the gas mixture through the tube;

(2) That when a mixture of hydrogen, carbon monoxide and air is passed through the U-tube, both the hydrogen and carbon monoxide (in the proportions in which he used them) burn completely without previous warming of the palladium asbestos. It is thus easily possible to determine hydrogen and carbon monoxide by combustion over palladium asbestos, and ascertaining the contraction and the volume of carbon dioxide formed;

(3) That the combustion of carbon monoxide under the above conditions begins at 120°, while that of methane does not begin

¹ *Z. analyt. Ch.*, 48 (1909), 232.

below 150° , and that if a mixture of hydrogen, carbon monoxide, methane and air is passed through the palladium asbestos tube, at a speed not exceeding one liter per hour, hydrogen and carbon monoxide will be completely oxidized and methane will not be attacked. If the speed of flow of the gas mixture be increased, the rise of temperature in the U-tube, resulting from the more active combustion, may cause some of the methane to burn and thus render the results worthless.

Nesmjelow then describes a method, original with him, for the fractional combustion of carbon monoxide by means of copper oxide. Copper oxide, mixed with asbestos fibers, is heated to dark redness and, after cooling in a desiccator, is placed in a small U-tube of hard glass. This is connected at the two ends with a gas burette and pipette in the usual manner, and a sand bath is then brought up under it and the lower part of the tube is covered with the sand. The bath is heated to 250° , and the mixture of hydrogen, carbon monoxide, methane and air passed through it about six times. The sand bath is then removed and the gas cooled to the temperature that it had at the beginning. The volume is measured and then the carbon dioxide that has been formed is determined by absorption. From these data the carbon monoxide and the hydrogen (which of course burns also) are calculated. At the above temperature methane is not oxidized. The speed of flow of the gases through the U-tube has no effect upon the accuracy of the separation.

METHANE (CH_4)

Marsh-gas — Fire-damp

Properties of Methane. — Specific gravity, 0.5539; weight of one liter, 0.7160 gram.

According to Bunsen, 1 volume of water absorbs at a temperature t ,

$$0.05449 - 0.0011807 t + 0.000010278 t^2;$$

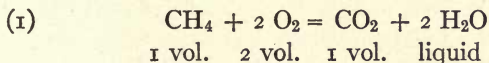
hence at 20° , 0.03499 volume.

One volume of alcohol absorbs at temperature t ,

$$0.522586 - 0.0028655 t + 0.0000142 t^2;$$

hence at 20° , 0.47096 volume.

Determination of Methane. — Methane may be determined by explosion with oxygen or air (see p. 141), by combustion with copper oxide (see p. 200), by combustion in the Drehschmidt platinum capillary tube (see p. 154) or by combustion in the Dennis pipette (see p. 148).



The amount of methane may be ascertained either by determining the volume of carbon dioxide that is formed, which will equal the volume of the methane, or by absorbing the carbon dioxide without measuring it and ascertaining the total diminution in volume, $\frac{1}{3}$ of which will equal the volume of the methane.

In the opinion of the author the method of determining methane with the combustion pipette is superior (a) to the explosion method because it permits of the combustion of the total residue and avoids the possibility of error through formation of oxides of nitrogen; (b) to the combustion with copper oxide because the latter calls for high and prolonged heating of the combustion tube; (c) and to the combustion with the Drehschmidt capillary because this method necessitates the use of a comparatively large volume of an explosive gas mixture, and further because of the tendency of the Drehschmidt tube to show leakage after a short period of use.

The combustion pipette and its level-bulb may be filled with water if no gases other than methane and nitrogen are present in the gas mixture; the methane is here determined by passing the gases, after combustion, into a potassium hydroxide pi-

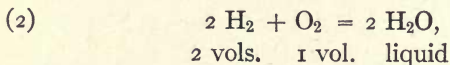
pette to completely remove the carbon dioxide and then calculating the methane from the total diminution in volume (see above).

If the combustion pipette and its level-bulb are filled with mercury and the gases are measured over mercury, then hydrogen, methane and nitrogen may be determined simultaneously by a single combustion by measuring the contraction after combustion and the volume of carbon dioxide that is formed.

A measured volume of the gas mixture is transferred to the combustion pipette and is burned in the usual manner by the slow addition of a measured amount of oxygen (see p. 149). The residual gas is then passed back into the burette and the contraction in volume is measured. The gas mixture is next passed into the potassium hydroxide pipette to absorb the carbon dioxide and is then again drawn back into the burette and measured.

Since one volume of methane produces, on combustion, one volume of carbon dioxide (see Equation 1), the volume of the methane in the gas mixture is equal to the volume of carbon dioxide formed.

Since



the contraction due to the combustion of hydrogen is equal to $\frac{3}{2}$ the volume of hydrogen in the gas mixture. The contraction due to the combustion of methane (see Equation 1) is equal to twice the volume of the carbon dioxide formed. Consequently the total contraction in the gas volume that results when a mixture of hydrogen and methane is burned may be represented by the expression

$$\text{Contraction} = \frac{3}{2} \text{ H}_2 + 2 \text{ CO}_2$$

$$\text{or} \quad \frac{3}{2} \text{ H}_2 = \text{Contraction} - 2 \text{ CO}_2$$

$$\text{or} \quad \text{vol. H}_2 = \frac{2}{3} (\text{Contraction} - 2 \text{ CO}_2)$$

The volume of hydrogen in the gas mixture is therefore found by subtracting twice the volume of carbon dioxide formed in the combustion from the total contraction, and taking $\frac{2}{3}$ of the remainder.

The following analyses, taken from actual practice, show the order in which the various measurements are made, and illustrate the accuracy of the determination with the combustion pipette.

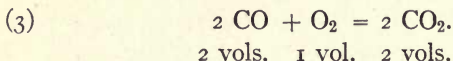
	I	II	III	IV	V
	cc.	cc.	cc.	cc.	cc.
Gas residue taken	61.4	64.50	67.00	64.0	65.7
Oxygen taken	98.5	96.55	98.55	97.6	100.0
Total	159.9	161.05	165.55	161.6	165.7
Residue after combustion	58.8	54.95	55.30	56.3	57.6
Contraction	101.1	106.10	110.25	105.3	108.1
Residue after absorbing CO ₂ in KOH pipette	34.3	29.15	28.60	30.7	31.4
Carbon dioxide found	24.5	25.80	26.70	25.6	26.2
	Per cent	Per cent	Per cent	Per cent	Per cent
Hydrogen	56.4	56.30	56.60	56.4	56.5
Methane	39.9	40.00	39.90	40.0	39.9
Nitrogen (diff.)	3.7	3.70	3.50	3.6	3.6

Hydrogen, methane, carbon monoxide and nitrogen may be determined by a single combustion if, in addition to the measurement of the total contraction and of the volume of carbon dioxide formed, the volume of oxygen consumed in the combustion is ascertained.

The combustion is carried on exactly in the manner described above for a mixture of hydrogen, methane and nitrogen except that after the carbon dioxide has been absorbed and the residue measured, the excess of oxygen is determined by passing the gas residue into a pipette containing alkaline pyrogallol or sodium hyposulphite and subtracting this result from the total volume of oxygen added. The difference is the oxygen consumed in the combustion. Having thus ascertained the contraction resulting from the combustion, the volume of carbon dioxide formed, and

the amount of oxygen consumed, we have all the data necessary for the calculation of the amounts of carbon monoxide, hydrogen, methane and nitrogen existing in the original mixture.

The volume changes that result from the combustion of hydrogen and methane are shown in Equations 1 and 2 on pages 241 and 242. When carbon monoxide is burned, two volumes of the gas unite with one volume of oxygen to form two volumes of carbon dioxide.



From these three equations the following expressions may be derived:

$$\text{Contraction} = \frac{1}{2} \text{ CO} + \frac{3}{2} \text{ H}_2 + 2 \text{ CH}_4.$$

$$\text{Carbon dioxide formed} = \text{CO} + \text{CH}_4.$$

$$\text{Oxygen consumed} = \frac{1}{2} \text{ CO} + \frac{1}{2} \text{ H}_2 + 2 \text{ CH}_4.$$

From these last three equations a variety of formulas for the calculation of the various components of the original mixture may be derived. Noyes and Shepard give —

$$(1) \text{ H}_2 = \text{Contraction minus oxygen consumed.}$$

$$(2) \text{ CO} = \frac{2}{3} (2 \text{ CO}_2 + \frac{1}{2} \text{ H}_2 \text{ minus oxygen consumed}).$$

$$(3) \text{ CH}_4 = \text{CO}_2 - \text{CO}.$$

$$(4) \text{ N}_2 = \text{Original volume} - (\text{H}_2 + \text{CO} + \text{CH}_4).$$

Instead of (2) and (3) we may also use —

$$\text{CO} = \text{CO}_2 - \text{CH}_4.$$

$$\text{CH}_4 = \frac{2 \text{ Contraction} - \text{CO}_2 - 3 \text{ H}_2}{3}$$

If no nitrogen is present in the original mixture the following equations of Vignon may be employed, V representing the volume of the gas mixture taken for the combustion.

$$\text{H}_2 = V - \text{CO}_2.$$

$$\text{CO} = \frac{1}{3} \text{CO}_2 + V - \frac{2}{3} \text{contraction.}$$

$$\text{CH}_4 = \frac{2}{3} \text{CO}_2 + \frac{2}{3} \text{contraction} - V.$$

The following analyses, taken from actual practice, illustrate the determination of carbon monoxide, hydrogen and methane by this method. The determination of nitrogen "by difference," after the removal of the absorbable and combustible constituents, does not yield accurate results. It is distinctly preferable to ascertain directly the amount of nitrogen in the gas mixture by the method outlined on p. 317.

	I	II	III	IV
	cc.	cc.	cc.	cc.
Volume of gas residue taken	83.45	85.05	83.05	86.95
Oxygen added	97.65	96.25	97.90	99.95
Total	181.10	181.30	180.95	186.90
Volume after combustion	49.30	46.95	49.75	49.50
Contraction resulting from combustion	131.80	134.35	131.20	137.40
Volume after absorption of carbon dioxide	13.05	10.15	13.75	12.00
Volume of carbon dioxide formed in the combustion	36.25	36.80	36.00	37.50
Volume after absorption of excess of oxygen	2.53	2.60	2.45	2.62
Oxygen in excess	10.52	7.55	11.30	9.38
Oxygen consumed in combustion of CO, H ₂ , and CH ₄	87.13	88.70	86.60	90.57

From the above experimental results the calculated percentages of the various gases are as follows: —

	I	II	III	IV
	Per cent	Per cent	Per cent	Per cent
Carbon monoxide	6.2	6.1	6.2	6.0
Hydrogen	53.5	53.7	53.7	53.9
Methane	37.3	37.2	37.2	37.1
Nitrogen (difference)	3.0	3.0	2.9	3.0

In a recent article ¹ Hempel states that he has found it difficult to obtain complete combustion of methane with the Dennis combustion pipette when methane is mixed with nitrogen. He asseverates that when the ordinary procedure is followed, a part of the methane may escape combustion, and that for complete combustion it is necessary to maintain the spiral at red heat for a considerable length of time, which causes surface oxidation of the mercury in the pipette, and, as a consequence, too high contraction. There is no doubt that this error would result if the spiral were subjected to prolonged heating, but experience of several years with the combustion pipette leads the author to believe that the maintenance of the spiral at red heat for sixty seconds after the introduction of the gas suffices in all cases for complete combustion of the methane, a statement that seems to be borne out by the analyses given on pages 243 and 245 and many others that might be cited. When the spiral is heated for so brief a time no appreciable oxidation of the mercury in the pipette results.

THE HEAVY HYDROCARBONS

As used in technical gas analysis, the term "heavy hydrocarbons" comprises gases of the series C_nH_{2n} (the olefines), such as ethylene, C_2H_4 , propylene, C_3H_6 , and butylene, C_4H_8 ; of the series C_nH_{2n-2} , such as acetylene, C_2H_2 ; and of the series C_nH_{2n-6} , such as benzol (benzene), C_6H_6 , and toluol (toluene) C_7H_8 .

The heavy hydrocarbons are the chief illuminants in coal gas or carburetted gas, and for this reason their determination is of importance when the gas is to be used directly for illuminating purposes.

Absorption of Heavy Hydrocarbons.—All of these gases are absorbed by fuming sulphuric acid of about 1.94 specific gravity containing about 24% free sulphur trioxide at 15°. The acid is placed in a special absorption pipette of the form shown in

¹ *Zeit. f. angew. Chem.*, 36 (1912), 1841.

Fig. 86. The small upper absorption bulb *B* is about 5 cm. in diameter and is filled by the glass-blower with pieces of broken glass which serves to increase the surface of contact between the gas and the acid. When broken glass is used in gas pipettes there is danger that some gas may be trapped between the pieces of glass. This may usually be avoided by drawing up the liquid very slowly in the bulb that contains the broken glass. The fuming sulphuric acid is introduced into the pipette through *A*. When the pipette is not in use *A* and *C* are covered with small glass caps made from glass tubing.

To effect the removal of the heavy hydrocarbons, the glass caps on the pipette are removed, and a short piece of small rubber tubing, such as is used on the other gas pipettes, is slipped upon *C*. A pinchcock is placed upon this rubber tube. The acid

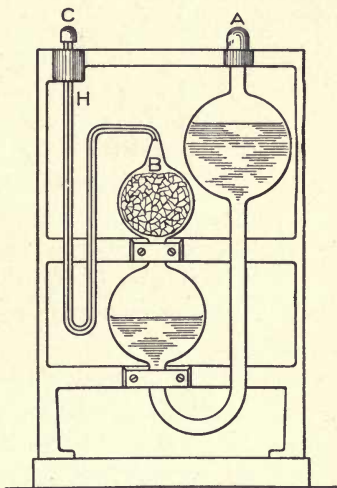


FIG. 86

in the pipette is driven up in the capillary to the point marked *H* by blowing through a rubber tube that has been attached to the end *A*, and the pinchcock is closed. The pipette and gas burette are then connected by an empty, dry capillary tube of the usual form. The gas mixture is then slowly passed over into the pipette, and after a few seconds is slowly drawn back into the burette. This is repeated three times or more, the number of passages of the gas depending upon the per cent of the heavy hydrocarbons present and the strength of the acid. Throughout the operation the fuming sulphuric acid should never be drawn above the point *H* in the capillary of the pipette. When the gas is drawn back into the burette the last time, the acid in the

pipette should be brought exactly to the point *H*. The pinch-cock at the top of the burette is now closed. The diminution in the gas volume may not yet be read off on the burette because of the presence in the gas of sulphur trioxide from the fuming acid in the pipette. This, together with any sulphur dioxide that may have been formed during the absorption, is removed by passing the gases into a pipette filled with potassium hydroxide (see p. 225). Then gas is then drawn back into the burette and the decrease in volume noted.

The moisture content of the gas, after it has been brought into contact with the fuming sulphuric acid and the potassium hydroxide, will of course be less than at the beginning of the determination when the gas was "saturated" with water vapor. To avoid error from this cause in the final measurement the gas must in this, as in all other similar absorptions, finally be read over water or over mercury upon which stands a drop of water.

This method of manipulation introduces slight errors in the results for those gases that are determined after the heavy hydrocarbons are removed, because the connecting capillary tube and the upper part of the capillary of the pipette are filled with air when the burette and pipette are connected. The volume of air in the capillaries is, however, so small¹ that the errors arising from this source may be disregarded in technical analyses.

ETHYLENE (C_2H_4)

Properties of Ethylene. — Specific gravity, 0.9684; weight of one liter, 1.2520 grams.

One volume of water absorbs at temperature *t*,

$$0.25629 - 0.00913631 t + 0.000188108 t^2;$$

hence at 20°, 0.1488 volume (Bunsen).

¹ The length of the empty capillary tube need not exceed 16 cm. which has a volume of only 0.16 cc.

One volume of alcohol absorbs at t° ,

$$3.59498 - 0.057716 t + 0.0006812 t^2;$$

hence at 20° , 2.7131 volumes (Carius).

Ether absorbs about twice its volume, turpentine oil and petroleum two and a half times their volumes, and olive oil its own volume of ethylene.

Determination of Ethylene by Absorption.—Bromine water absorbs the gas rapidly and completely;¹ the vapor of bromine must be removed after the absorption by passing the gas into a potassium hydroxide pipette. The reagent is prepared by diluting saturated bromine water with twice its volume of water. It then contains about one per cent of bromine. The liquid is placed in a Hempel double absorption pipette for liquid reagents (Fig. 36) with water in the last two bulbs.

The usual absorbent for ethylene is fuming sulphuric acid, ethionic acid, $C_2H_6S_2O_7$, being formed. The determination is carried out in the manner described on p. 247.

Determination of Ethylene in presence of Acetylene.—Tucker and Moody state² that ethylene may be determined in mixture with acetylene by passing the gases through an ammoniacal silver solution which removes acetylene completely but absorbs only a relatively small amount of ethylene. The method is not exact but it might prove useful in an approximation of the percentages of ethylene and acetylene in a mixture of the two gases. The ammoniacal silver solution that is used in this separation is prepared by dissolving 10 grams of silver nitrate in 500 cc. of distilled water, adding dilute hydrochloric acid until the solution is barely acid to litmus paper, and then adding ammonium hydroxide until the solution is slightly ammoniacal. When acetylene is absorbed by this solution, silver acetylides, Ag_2C_2 , is formed.

¹ Treadwell and Stokes, *Berichte der deutschen chemischen Gesellschaft*, **21** (1888), 3131; Haber and Oechelhäuser, *ibid.*, **29** (1896), 2700.

² *J. Am. Chem. Soc.*, **23** (1901), 671.

Separation of Ethylene from Benzene. — The separation of ethylene from benzene may, according to Haber and Oechelhäuser,¹ be accomplished by means of bromine water which removes the ethylene completely but does not appreciably attack the benzene if the contact between gas and reagent is not prolonged beyond two minutes. Some benzene vapor is, however, mechanically carried down by the bromine vapor, and for this reason the method does not yield very accurate results.

Separation of Ethylene from Butylene. — Fritzsche states² that ethylene may be volumetrically separated from butylene by means of sulphuric acid of 1.62 specific gravity which absorbs butylene but not ethylene.

PROPYLENE (C_3H_6)

Specific gravity, 1.4527; weight of one liter, 1.878 grams.

The gas may be determined by absorption with fuming sulphuric acid or by combustion. Details of these methods are given on pages 247 and 149.

ACETYLENE (C_2H_2)

Properties of Acetylene. — Specific gravity, 0.8988; weight of one liter, 1.1620 grams.

Acetylene is quite soluble in a number of liquids, as is shown in the following table:³

		at 12° and 755 mm.	
1 vol. saturated salt solution	dissolves	0.23 vol. acetylene	
1 " water		1.18 "	"
		at 18° and 760 mm.	
1 vol. carbon disulphide	dissolves	1.0 vol. acetylene	
1 " oil of turpentine	"	2.0 "	"
1 " carbon tetrachloride	"	2.0 "	"

¹ *J. f. Gasbeleuchtung*, 39 (1896), 799; 43 (1900), 347.

² *Z. f. angew. Chem.*, 1896, 456.

³ Vogel, *Handbuch für Acetylen*, p. 152.

			at 18° and 760 mm.	
1 vol. amyl alcohol	dissolved	3.5 vol. acetylene		
1 " styrol	"	3.5	"	"
1 " chloroform	"	4.0	"	"
1 " benzene	"	4.0	"	"
1 " absolute alcohol	"	6.0	"	"
1 " acetic acid	"	6.0	"	"
1 " acetone	"	25	"	"

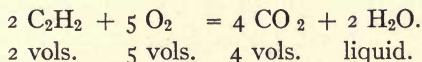
			at 15° and 12 atm.	
1 " acetone	"	300 vol. acetylene		

			at - 80° and 760 mm.	
1 " acetone	"	2000 vol. acetylene		

It is slowly absorbed by concentrated sulphuric acid, acetyl sulphonic acid, $C_2H_4SO_4$, being formed. An ammoniacal solution of cuprous chloride absorbs the gas rapidly and there is formed a brown to violet-red precipitate of copper acetylide, Cu_2C_2 , which explodes when heated or struck. Acetylene produces in an ammoniacal silver solution ¹ a white precipitate, Ag_2C_2 , which is even more explosive than the copper acetylide. If the gas is led into ammoniacal solutions of aurous thiosulphate or potassium mercuric iodide, exceptionally explosive compounds are formed.

All of the ammoniacal solutions of metals that have been mentioned may be used as absorbents for acetylene.

Determination of Acetylene. — Although acetylene may be determined by combustion with oxygen, this method cannot usually be employed because the gas occurs in mixtures with other combustible gases. One volume of acetylene yields on combustion 2 volumes of carbon dioxide. When 2 volumes of acetylene are burned there is a contraction of 3 volumes.



¹ The method of preparing this solution is described under Ethylene, p. 249.

It is best determined by leading it through an ammoniacal cuprous chloride solution, a reddish brown precipitate being thrown down. The precipitate is filtered off, and is washed with water containing ammonia until the wash-water passes through colorless. The moist copper acetylide may be collected in a Gooch crucible and dried over calcium chloride at 100° in a current of carbon dioxide¹ and weighed as Cu_2C_2 . Dry copper acetylide may, however, explode at a temperature as low as 60° .

The acetylene may be determined, without danger of explosion, by taking advantage of the fact that the moist precipitate contains carbon and copper² in the atomic proportion of 1:1, and determining the copper in the moist compound. This is done by pouring hydrochloric acid upon the precipitate which is thereby decomposed with evolution of acetylene. As it is difficult to completely decompose the copper acetylide, the end of the reaction is not waited for, but the rest of the precipitate, without being washed, is dried on the filter and ignited. The copper oxide is dissolved in a few drops of nitric acid, and this solution is added to the hydrochloric acid filtrate first obtained. The copper in the solution may then be determined electrolytically, or it may be precipitated from hot solution with sodium hydroxide, filtered off, washed, ignited and weighed as cupric oxide.

Acetylene may be determined volumetrically in the Hempel apparatus by absorbing it with fuming sulphuric acid contained in the pipette shown in Fig. 86. It is necessary to pass the gas repeatedly into the pipette until no further diminution in volume is noted upon measuring the residual gas in the burette. Before making the final measurement, the gas must, of course, be passed into the potassium hydroxide pipette to remove the sulphur trioxide. Traces of acetylene may still remain in the gas mixture after this treatment with fuming sul-

¹ Scheiber, *Z. analyt. Chem.*, **48** (1909), 537.

² Scheiber, *Ber. d. deutsch. Chem., Ges.* **41** (1908), 3816.

phuric acid, and these may be removed by passing the gas into a pipette containing an ammoniacal cuprous chloride solution. If oxygen is present with the acetylene, it is removed, after the treatment of a gas mixture with fuming sulphuric acid, by absorption with alkaline pyrogallol. Phosphorus cannot be used for the absorption of oxygen in the presence of even very small amounts of acetylene because the gas inhibits the union between oxygen and phosphorus to such an extent as to render it impossible to obtain even approximately correct results for oxygen with this reagent.

BENZENE (C_6H_6)

Specific gravity at 15° , 0.885. Melting-point, about 6° . Boiling-point, 80.3° .

Determination of Benzene. — Benzene is rapidly absorbed by fuming sulphuric acid and this reagent may be employed for the determination of the gas if no other heavy hydrocarbons are present. This, however, is rarely the case, and the importance of benzene as an illuminant renders very desirable the perfection of a method for the accurate volumetric separation and determination of benzene vapor in the presence of other of the heavy hydrocarbons.

Absorption of Benzene by Alcohol. — In 1891 Hempel and Dennis¹ proposed a method for the removal of the benzene vapor that was based on the ready absorption of that substance by absolute alcohol. They used a mercury pipette (Fig. 50) that contained above the mercury 1 cc. of absolute alcohol that was first saturated with the illuminating gas under examination. After the removal of the benzene the residual alcohol vapor was absorbed by passing the gas residue into a mercury pipette containing 1 cc. of water.

Further examination² of this method demonstrated, however, that the removal of benzene vapor by alcohol is not complete

¹ *Berichte der deutschen chemischen Gesellschaft*, 24 (1891), 1162.

² Dennis and O'Neill, *Jour. Am. Chem. Soc.*, 25 (1903), 503.

and that furthermore the solubility of various gases in alcohol ¹ is so appreciable that errors arising from this cause cannot be entirely eliminated by saturation of the alcohol with these gases.

Absorption of Benzene by Paraffin Oil. — The removal of benzene by cooled paraffin oil was proposed by Müller.² The gas mixture is first dried by passing it through apparatus containing calcium chloride and is then slowly passed through an absorption apparatus containing liquid paraffin of 0.88 to 0.89 specific gravity and of a boiling-point of about 360°. The absorption apparatus is weighed before the experiment, is cooled during the experiment with a freezing mixture of ice and salt, and after the absorption is brought to room temperature and again weighed. The amount of gas that is passed through the absorbent is measured by a gas meter placed after the absorption apparatus.

Determination of Benzene as Dinitrobenzene. — Harbeck and Lunge ³ devised a method for the determination of benzene that is based upon the fact that benzene, when present in a gas mixture in relatively small amount, is quantitatively converted into dinitrobenzene when the gases are passed through a suitable absorption apparatus containing a mixture of equal weights of concentrated sulphuric acid and fuming nitric acid. The dinitrobenzene, which is difficultly soluble in water but easily soluble in ether, is extracted with ether and, after evaporation of the solvent, is weighed. From this weight the amount of benzene in the gas is calculated. The method is quite accurate, but unfortunately it is so time-consuming as to preclude its use in routine analysis.

Pfeiffer determines ⁴ the dinitrobenzene obtained by the Harbeck and Lunge method by a volumetric procedure based upon

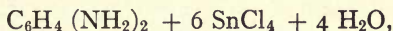
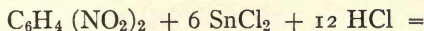
¹ See Lunge, *Chemisch-technische Untersuchungsmethoden*, 2, 585.

² *J. f. Gasbeleuchtung*, 41 (1898), 433.

³ *Z. f. anorg. Chem.*, 16 (1898), 41; also *Chemisch-technische Untersuchungsmethoden*, 2, 592.

⁴ *Chemiker-Zeitung*, 28 (1904), 884.

the reaction first mentioned by Limpricht ¹ in which the dinitrobenzene is reduced to diamidobenzene by stannous chloride and the excess of the reducing agent is determined by titration with an iodine solution of known strength. The reactions involved are



Separation of Benzene from Ethylene.—In the method of Haber and Oechelhäuser ² the total amount of the heavy hydrocarbons is determined by means of fuming sulphuric acid and the ethylene in another sample is determined by absorption in bromine water of known strength and titration of the residual free bromine with sodium thiosulphate. Assuming that only benzene and ethylene are present the amount of benzene is equal to the difference between these two results.

The method gives fairly accurate results, but it is open to the objection that, for benzene, it is indirect and that a determination takes considerable time.

Absorption of Benzene with Nickel Solution.—Dennis and O'Neill ³ developed a gas volumetric method for the determination of benzene that is based upon the reaction that takes place when nickel cyanide, ammonia and benzene are brought together, the compound $\text{Ni}(\text{CN})_2 \cdot \text{NH}_3 \cdot \text{C}_6\text{H}_6$ being formed.⁴ The absorbent for benzene was first prepared by dissolving nickel nitrate in water and pouring this solution into ammonium hydroxide. The resulting solution had a slight odor of ammonia. The reagent was placed in a Hempel simple absorption pipette, the gas mixture was run into the pipette and the gas shaken with the reagent for three minutes. It was then drawn back into the

¹ *Ber. d. deutsch. chem. Ges.*, **11** (1878), 35.

² *Jour. f. Gasbeleuchtung*, **39** (1896), 799; **43** (1900), 347.

³ *J. Am. Chem. Soc.*, **25** (1903), 503.

⁴ Hofmann and Küspert, *Z. f. anorg. Chem.*, **15** (1897), 204.

burette, passed into a pipette containing mercury and 5 cc. of a 5% solution of sulphuric acid to remove ammonia, after which it was drawn back and finally measured. The results obtained with this method by different analysts were, however, quite discordant. Some chemists found the method to be very accurate while others reported it to be far from satisfactory. A careful examination of the statements from different analysts rendered it probable that those samples of illuminating gas with which the method gave good results contain the cyanogen compounds necessary to the formation of the product described by Hofmann and Küspert, and that the poor results on other samples of illuminating gas might be due to the absence of cyanogen compounds in the gas. Consequently the solution of ammonia nickel nitrate was replaced¹ by a solution of ammonia nickel cyanide. This reagent was found to rapidly and quantitatively absorb benzene from mixtures of benzene vapor with air as well as from samples of illuminating gas, and it was further demonstrated that ethylene was not taken up by the solution. The reagent is prepared as follows:

To 50 grams of nickel sulphate ($\text{NiSO}_4 \cdot 7 \text{H}_2\text{O}$), dissolved in 75 cc. of water, is added 25 grams of potassium cyanide dissolved in 40 cc. of water. After the addition of 125 cc. of ammonium hydroxide (Sp. Gr. 0.9) the mixture is shaken until the nickel cyanide has completely dissolved. It is then cooled to 0°C . and allowed to stand at that temperature for twenty minutes. The clear liquid is decanted from the crystals of potassium sulphate that have separated, and is treated with a solution prepared by dissolving 18 grams of crystallized citric acid in 10 cc. of water. After the mixture has stood again at 0° for ten minutes, the greenish blue supernatant solution is decanted and is introduced into a gas pipette. Two drops of liquid benzene are now added to the reagent and the pipette is shaken until the benzene has combined with the reagent, which is evidenced by the appearance of a fine, granular, white precipitate in the pipette. This is

¹ Dennis and McCarthy, *Jour. Am. Chem. Soc.*, 30 (1908), 233.

effected in two or three minutes. This addition of benzene to the reagent is made because it has been found that a freshly prepared solution of the ammonia nickel cyanide does not actively remove benzene vapor until some of the compound between benzene and the reagent has been formed.

The reagent is placed in a Hempel double gas pipette for solid reagents (Fig. 37) the large bulb of the pipette being filled with broken glass. The absorbent is brought into the first two bulbs, and water is introduced into the third and fourth bulbs. The analytical absorbing power of the reagent is 5; consequently 100 cc. of the reagent in the pipette may be used in analytical work for the absorption of 500 cc. of benzene vapor.

In determining benzene by this method a gas sample is measured off in a gas burette which is then connected by means of the usual capillary tube with the pipette containing the ammonia nickel cyanide solution. The gas mixture is repeatedly passed over into the pipette and drawn back into the burette during a period of about three minutes, which will suffice for the removal of the benzene in amounts up to about eight per cent. The gas is finally drawn into the burette which is then joined to a double pipette of the form shown in Fig. 37. The bulb *A* is filled with glass tubes and *A* and *B* are then charged with a five per cent solution of sulphuric acid. Bulbs *C* and *D* are filled with sufficient water to protect the reagent from the air. The gas residue is now passed back and forth about two minutes to remove the ammonia that enters the gas mixture from the reagent. If mercury is used as the confining liquid in the burette the small amount of water that usually covers its surface will absorb ammonia from the reagent. This may rapidly be removed by drawing into the burette from the pipette sufficient dilute sulphuric acid to completely neutralize the ammonium hydroxide thus formed and then driving the acid back into the burette.

Both reagents must of course first be shaken with samples of the gas mixture under analysis in order to saturate the absorb-

ents with those constituents of the mixture which they do not absorb.

The majority of those who have used this method in technical practice have found that it gives uniform and accurate results.¹

On the other hand, some report that even in its modified form the method is not satisfactory. In the greater number of such cases, correspondence with the analyst has developed either that the reagent was not properly prepared or that the absorption apparatus was of an inefficient type. But little weight can be attached to the criticism of the method by Harding and Taylor² because of the unconvincing character of the experimental work of those authors. They compared the results by the ammonia nickel cyanide method with those obtained by another method of dubious accuracy,³ using a gas mixture of unknown benzene content, and they assume that differences in the results are due to the inaccuracy of the first named method. They further found that prolonged contact between the gas mixture and the ammonia nickel cyanide and dilute sulphuric acid caused a slow but steady diminution of the gas volume and they ascribed this to the absorption by the reagent of hydrocarbons other than benzene.

To test the correctness of this assumption and to ascertain whether, as Harding and Taylor maintain, there is slow but continuous absorption of gas upon repeated passage of the residue into ammonia nickel cyanide and 5 per cent sulphuric acid, the following experiments were carried out in the author's laboratory by Mr. E. L. Davies. Mr. Davies placed the solution of ammonia nickel cyanide and of 5 per cent sulphuric acid in the double Hempel pipettes above mentioned and passed into these pipettes samples of the city gas of Ithaca, which is a mixture of coal gas and carburetted water gas. Carbon dioxide

¹ See, for example, Pfeiffer, *Z. f. angew. Chem.*, **20** (1907), 22; Stavorinus, *Hel Gas*, 1905, p. 554; *J. f. Gasbeleuchtung*, **49** (1906), 272.

² *Jour. Ind. and Eng. Chem.*, **2** (1910), 345.

³ See Haber, *Jour. f. Gasbeleuchtung*, **43** (1900), 511.

was of course first removed from the gas by means of potassium hydroxide. He obtained the results that are tabulated below.

	May 27, 1912	May 28, 1912	May 29, 1912
Volume of residue after removal CO ₂ . . .	96.8 cc.	97.0 cc.	96.8 cc.
Volume after 3 minutes treatment with nickel solution and 7 minutes treatment with 5% H ₂ SO ₄	93.6 cc.	94.2 cc.	94 cc.
Volume after first repetition with these two reagents	93.6 cc.	94.2 cc.	94 cc.
Volume after 2d repetition	93.6 cc.	94.2 cc.	94 cc.
" " 3d "	93.5 cc.	94.2 cc.	94 cc.
" " 4th "	93.5 cc.	94.2 cc.	94 cc.
" " 5th "		94.2 cc.	94 cc.
" " 6th "		94.2 cc.	94.1 cc.
Total duration of contact with nickel solu- tion	18 min.	24 min.	18 min.
Total duration of contact with 5% H ₂ SO ₄	42 min.	56 min.	42 min.
Total duration of contact with both re- agents	60 min.	80 min.	60 min.

The above analyses appear to demonstrate conclusively that the solutions of ammonia nickel cyanide and 5 per cent sulphuric acid do not gradually absorb constituents of the gas mixture other than benzene.

The results of the experiments with ethylene described by Harding and Taylor are directly contradictory to those cited by Dennis and McCarthy and are probably incorrect both because of impurities in the ethylene that was used and because of solution and escape of the gas through the single outer bulb. That they find that a gas mixture containing ethylene diminishes in volume when shaken with ammonia nickel cyanide for even so short a time as one or two minutes is but natural, because in this as in all other cases in gas analysis a liquid reagent will dissolve somewhat of a gas and must be saturated with the gas before the analysis is made.¹ That acetylene dissolves both in the reagent

¹ See Dennis and McCarthy, *loc. cit.*, p. 238.

and in the 5% sulphuric acid is not at all surprising because that gas is quite soluble even in distilled water. The point is quite beside the question in the present case because acetylene does not occur as a constituent of ordinary illuminating gas.

Stavorinus¹ subjected the method to a careful experimental examination and found that the reagent did not absorb air, hydrogen, carbon monoxide, methane, pentane, ethylene, or propylene. He continues, "Acetylene on the other hand was absorbed, which was to be expected, but since this gas is present in illuminating gas in scarcely detectable traces it may be disregarded. . . . Gases carburetted with benzene gave excellently agreeing results, and the method can furthermore be commended because of its simplicity of manipulation, and its speed."

NAPHTHALENE ($C_{10}H_8$)

Melting-point, 79° ; boiling-point, 218° .

Naphthalene is a white crystalline substance that is solid at ordinary temperatures. It is, however, quite volatile and for that reason its vapor is frequently present in carburetted gas.

Determination of Naphthalene. — For the determination of naphthalene in gas mixtures the method original with Colman and Smith,² and modified and improved by Gair,³ Rutten,⁴ Colman,⁵ Jorissen and Rutten,⁶ and Albrecht and Müller⁷ is almost exclusively employed. It is based upon the fact, first noted by Fritzche,⁸ that naphthalene unites with picric acid to form a crystalline compound of the formula $C_{10}H_8 \cdot C_6H_3N_3O_7$, which is but slightly soluble in a saturated or nearly saturated solution

¹ *Loc. cit.*

² *Jour. Soc. Chem. Ind.*, **19** (1900), 128.

³ *Jour. Soc. Chem. Ind.*, **24** (1905), 1279.

⁴ *Hel Gas*, 1908, Nos. 9 and 12.

⁵ *Jour. Soc. Chem. Ind.*, **28** (1909), 1179.

⁶ *Jour. f. Gasbeleuchtung*, **53** (1910), 269.

⁷ *Jour. f. Gasbeleuchtung*, **54** (1911), 592.

⁸ *Jour. prakt. Chem.*, **73** (1858), 282.

of picric acid. After absorption of the naphthalene, the excess of free picric acid is titrated with $\frac{N}{10}$ potassium hydroxide.

The determination may be carried out as follows:—

The gas mixture, which must be free from tar, cyanogen, hydrogen sulphide and ammonia,¹ is passed through two gas washing bottles containing a saturated solution of picric acid together with some undissolved picric acid. This absorbing solution is prepared by weighing off exactly 2.5 grams of picric acid, dividing this amount of the acid into two nearly equal portions, placing one portion in a gas washing bottle of 100 cc. capacity, adding 25 cc. of water and then shaking the bottle vigorously until a saturated solution of picric acid is formed. The other portion of the solid picric acid is then placed in a second gas washing bottle and treated in similar manner. The two bottles are then connected to each other glass to glass by rubber tubing, and the gas mixture is led through the absorbent at a rate of from 40 to 50 liters per hour. The total volume of gas passed through the picric acid is measured by a gas meter placed after the wash bottles and it should be such as will contain not less than 0.05 gram and not more than 0.20 gram of naphthalene.²

The contents of the two wash bottles including the undissolved picric acid is carefully transferred to a 250 cc. measuring flask, the wash bottles being rinsed with water. The stopper of the flask is inserted, and the flask is then heated on a water bath for half an hour, with frequent shaking, to from 40° to 50°. This will cause the complete solution of all of the picric acid.

In the meantime 2.5 grams of picric acid is weighed out into another 250 cc. measuring flask, is dissolved in water and is diluted to the mark; 200 cc. of this solution is then titrated with $\frac{N}{10}$ potassium hydroxide, lacmoid being used as indicator.

¹ See analysis of illuminating gas, p. 306.

² Albrecht and Müller, *loc. cit.*

The measuring flask that contains the picric acid by which the naphthalene has been absorbed is allowed to cool to the temperature of the room and is then filled to the mark with water, the contents thoroughly shaken, and 200 cc. of the solution is filtered off through a dry filter. This filtrate is then also titrated with $\frac{N}{10}$ potassium hydroxide. The difference in the number of cubic centimeters of potassium hydroxide used in the two titrations multiplied by $\frac{5}{4} \times 0.0128$ gives the grams of naphthalene absorbed by the picric acid in the two wash bottles. This amount is then calculated to grams of naphthalene per cubic meter of gas.

CYANOGEN (C_2N_2)

Properties of Cyanogen. — Specific gravity, 1.7993; weight of one liter, 2.3261 grams.

One volume of water dissolves at 20° , 4.5 volumes of cyanogen; 1 volume of alcohol, 20 volumes of cyanogen.

Burned with twice its volume of oxygen it forms 2 volumes of carbon dioxide and 1 volume of nitrogen.

Detection of Cyanogen. — Free cyanogen, or dicyanogen, may be detected according to Kunz-Krause¹ by the Schönbein-Pagenstecher reaction. For carrying out this test, strips of filter paper are first dipped into a dilute aqueous solution of copper sulphate (1:1000), and are then impregnated with a 3 per cent tincture of gum guaiac. The paper thus prepared turns blue when acted upon by dicyanogen or hydrocyanic acid, but this blue color is also caused by certain oxidizing agents such as ozone and nitric acid.

The reaction is somewhat sharper when the gas mixture, instead of being brought in contact with the paper above described, is passed through a wash bottle containing an alcoholic copper sulphate — gum guaiac solution.

The reaction has lately been increased in delicacy by E. Schaer, who uses guaiaconic acid in place of the gum guaiac.

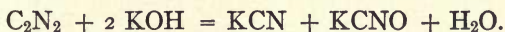
¹ *Zeitschr. angew. Chem.*, 26 (1901), 652.

The reagent should always be freshly prepared, and this is done by adding to 10 cc. of a dilute aqueous copper sulphate solution 15 cc. of alcohol in which a little guaiaconic acid has previously been dissolved.

Brünnich states¹ that the delicacy of the Schönbein-Pagenstecher test for hydrogen cyanide may be greatly enhanced by moistening the paper with formalin instead of with water before exposing the paper to the gas mixture under examination. The color that here results if hydrogen cyanide is present is deep blue, whereas, if the paper is moistened with water, it is a light blue.

Another delicate reaction for dicyanogen is given by Kunz-Krause in the article above cited, this test depending upon the formation of isopurpuric acid or picrocyaminic acid, $C_8H_5N_5O_6$, from picric acid. 2 cc. of a cold saturated aqueous solution of picric acid (1:86) is mixed with 18 cc. of alcohol and 5 cc. of a 15 per cent aqueous solution of potassium hydroxide. When brought into contact with this solution pure cyanogen yields a deep purple-red color, which later turns to brown. On long standing the potassium salt of isopurpuric acid separates in the form of an oil of purple-red color. This reagent also must always be freshly prepared.

Potassium hydroxide absorbs cyanogen, potassium cyanide and potassium cyanate being formed.

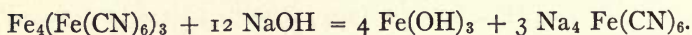


Determination of Cyanogen.—Cyanogen may be determined by the method of Nauss.² 100 liters of the gas mixture is passed at a rate of from 50 to 100 liters per hour through two absorption bottles in each of which is placed 20 cc. of a solution of ferrous sulphate (1:10) and 20 cc. of a solution of potassium hydroxide (1:3). After the passage of the gas, the contents of the absorption bottles is carefully rinsed into a 500 cc. flask,

¹ *Chemical News*, 87 (1903), 173.

² *J. Gasbeleuchtung*, 43 (1900), 696.

some potassium hydroxide in solution is added and then ferrous sulphate (1:10). If hydrogen sulphide is present, the solution of ferrous sulphate should be added until no further precipitation of black ferrous sulphide results. It is advisable to add also about one gram of lead carbonate to ensure the complete removal of hydrogen sulphide. The contents of the flask is then heated for some minutes and allowed to cool. The flask is filled to the mark, and 5 cc. more of water is added to compensate for the volume of the precipitate. After being vigorously shaken, the liquid is filtered off through a dry paper; 50 cc. of the filtrate is poured into an excess (20 to 30 cc.) of a hot solution of ferric alum that contains 200 grams of ferric alum to the liter. The solution is warmed for a short time on a water bath and Prussian blue is then precipitated by the addition of dilute sulphuric acid. The precipitate is collected on a folded filter in a hot-water funnel, and is washed with hot water until sulphuric acid has been completely removed. The precipitate with the filter is then at once placed in a flask, some water is added, and the liquid is heated to boiling, the contents of the flask being frequently shaken to loosen the precipitate from the paper. The amount of the Prussian blue is then directly determined by titration with a $\frac{1}{50}$ N solution of sodium hydroxide.



The solution of sodium hydroxide is added, a little at a time, until all of the Prussian blue is decomposed. The contents of the flask is kept hot during the addition of the sodium hydroxide for the purpose of hastening the reaction. The excess of sodium hydroxide is then ascertained by titrating back with $\frac{1}{50}$ N acid. The liquid must be continuously heated and frequently shaken during this last titration, for even in the presence of an excess of sodium hydroxide there is some re-formation of Prussian blue which causes a green coloration of the liquid. When the color changes to a light greenish yellow, the end point has been reached.

1 cc. $\frac{1}{50}$ N sodium hydroxide = 0.0007794 gram cyanogen.

Nauss found from 6 to 15 grams of cyanogen in 100 cubic meters of Karlsruhe gas after the last purifier.

Samtleben, using the analytical method of Nauss, found ¹ in coal gas of Bernburg from 155 to 301 grams of hydrogen cyanide in 100 cubic meters before the purifiers, and from 8.8 to 21.3 grams per 100 cubic meters after the purifiers.

Detection and Determination of Cyanogen in presence of Hydrogen Cyanide. — Wallis ² observed that when hydrogen cyanide is passed into an acidified solution of silver nitrate it reacts quantitatively with the silver nitrate to precipitate silver cyanide. He also states that cyanogen does not react with an acidified solution of silver nitrate, and that any cyanogen that dissolves as such in the reagent may be removed practically completely by passing a current of air through the solution. Upon this difference of behavior of cyanogen and hydrogen cyanide toward silver nitrate, Wallis bases a method for the detection of cyanogen and of hydrogen cyanide when these gases are present together in a gas mixture, but he carried the work no further than to show the applicability of this method to the qualitative examination of a few special gas mixtures.

Quite recently Rhodes has made a careful study of the reaction noted by Wallis and has developed a method ³ that permits both of the detection and of the accurate determination of cyanogen in the presence of hydrogen cyanide. For the detection of cyanogen in the presence of hydrogen cyanide he proceeds as follows —

Test tubes 15 cm. long and provided with side arms are used for the absorption of the gases. In one such tube is placed 10 cc. of a 10 per cent solution of silver nitrate to which one drop of dilute (6 N) nitric acid has been added. In the second tube is placed 10 cc. of a 2 N solution of potassium hydroxide. The two absorption tubes are connected in series and the gas mixture is

¹ *J. Gasbeleuchtung*, **49** (1906), 205.

² *Annalen* (Liebig) **345** (1906), 353.

³ *J. Ind. and Eng. Chem.*, **4** (1912), 652.

passed through them. The duration of the passage of the gas depends upon the amount of hydrogen cyanide in the gas mixture. Since the first tube is intended to hold back the hydrogen cyanide, the passage of the gas must of course be stopped before all of the silver nitrate in this tube is converted into silver cyanide. After the gas mixture has been passed through the absorption tubes for a sufficient length of time, it is replaced by a current of air which is continued for about ten minutes. The second absorption tube, which contains the solution of potassium hydroxide, is then disconnected and 5 cc. of a solution of ferrous sulphate and one drop of a solution of ferric chloride are added to the contents of the tube. After about fifteen minutes there is added dilute sulphuric acid in amount sufficient to dissolve the ferrous and ferric hydroxides. The appearance of a blue precipitate or of a distinct green color in the solution after acidification proves the presence of cyanogen in the original gas mixture. The delicacy of this reaction for cyanogen is shown by the results in the following table: —

VOLUME OF CYANOGEN	COLOR DEVELOPED
10. cc.	Blue precipitate
5. cc.	Blue precipitate
1. cc.	Blue precipitate
0.4 cc.	Green color
0.3 cc.	Faint green color
0.2 cc.	Very faint green color

From the above data it appears that as small an amount as 0.3 cc. of cyanogen may be detected in this manner. That the presence of hydrogen cyanide in the gas does not interfere with the delicacy of this method was demonstrated by passing through the absorbents a mixture of 0.4 cc. of cyanogen and 10 cc. of hydrogen cyanide and obtaining a distinct reaction for cyanogen under these conditions.

Since potassium cyanide is hydrolyzed to a considerable degree in aqueous solution with the formation of hydrocyanic acid,

it was thought possible that the passage of a large volume of air through the apparatus might carry with it some of the hydrogen cyanide, and thus decrease the delicacy of the test. It was found, however, that this was not the case, 0.4 cc. of cyanogen still yielding a distinct reaction when 20 liters of air was passed through the apparatus subsequent to the introduction of the cyanogen.

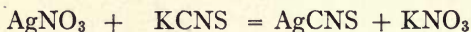
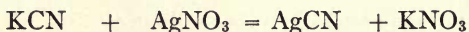
A small amount of carbon dioxide in the gas mixture under examination does not interfere with the test for cyanogen. But if an amount of gas containing carbon dioxide sufficient to convert all of the potassium hydroxide into potassium carbonate is passed through the reagent, the reaction for cyanogen is then not obtained.

The presence of hydrogen cyanide in the original gas mixture is detected by collecting on a filter any precipitate that may have formed in the solution of silver nitrate in the first absorption tube, washing the precipitate with very dilute nitric acid, drying it, transferring it to a small sublimation tube, and warming it with a small amount, five milligrams or less, of iodine. The formation of a sublimate of cyanogen iodide on the side of the tube proves the presence of silver cyanide in the precipitate and consequently of hydrogen cyanide in the original gas mixture; 0.1 mg. of silver cyanide, equivalent to 0.02 mg. of hydrogen cyanide, may be detected in this manner.

To determine cyanogen and hydrogen cyanide in the presence of each other the gas mixture is passed through a series of four absorption test tubes. Each of the first two of these tubes contains 5 cc. of a standardized (approximately $\frac{N}{10}$) solution of silver nitrate and one drop of dilute nitric acid. In the third absorption tube is placed 10 cc. of an approximately 2 N solution of potassium hydroxide that is free from chloride, and the last tube contains 5 cc. of this solution. The gas mixture under examination is slowly passed through this absorption apparatus

or is carried through by a slow current of air. The first two absorption tubes are then disconnected and the solution of silver nitrate that they contain is transferred to a beaker and is filtered. The precipitate and filter paper are washed with very dilute nitric acid until free from soluble silver salts. The filtrate and wash water are then combined and are titrated with a standardized solution of ammonium sulphocyanate with ammonium ferric alum as indicator, and the amount of hydrogen cyanide that was present in the original gas mixture is calculated from the volume of ammonium sulphocyanate used.

The contents of the third and fourth absorption tubes is transferred to a beaker and a known volume of a standardized solution of silver nitrate is added. The silver nitrate must be in excess of the amount required to precipitate all of the potassium cyanide in the solution as silver cyanide. The solution and the suspended precipitate are then thoroughly stirred, and dilute nitric acid is next added until the precipitated silver oxide redissolves and the solution becomes slightly acid. The precipitate of silver cyanide is now filtered off, the precipitate and filter paper are washed with very dilute nitric acid until all soluble silver salts are removed, and the filtrate and wash water are combined and are titrated with a standardized solution of ammonium sulphocyanate with ammonium ferric alum as indicator. The cyanogen present in the original gas mixture is then calculated, the reactions involved in the calculation being:—



Analyses made by this method of mixtures of known amounts of cyanogen and hydrogen cyanide showed that the procedure gives very satisfactory results.

HYDROGEN CYANIDE (HCN)

Properties of Hydrogen Cyanide.— Specific gravity, 0.9359; weight of one liter, 1.2096 grams.

The gas is easily soluble in water and in alcohol, and is absorbed by potassium hydroxide with the formation of potassium cyanide.

Strong acids, especially hydrochloric acid and sulphuric acid, decompose hydrocyanic acid with formation of formic acid and ammonia.

Detection of Hydrogen Cyanide. — Hydrogen cyanide may be detected by absorbing the gas in a solution of potassium hydroxide, and then adding ferrous sulphate and one drop of ferric chloride to the solution of potassium cyanide. (If the solution that is being tested is not alkaline, potassium hydroxide should be added at this point.) The solution is then gently warmed and is acidified with hydrochloric acid. A dark blue precipitate of Prussian blue proves the presence of potassium cyanide in the absorbent. Since cyanogen is absorbed by potassium hydroxide with the formation of potassium cyanide, that gas will also give this reaction.

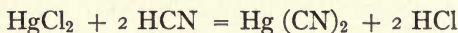
Another test for hydrocyanic acid is to add ammonium sulphide until the solution takes on a yellow color, then ammonia, — or, better, a drop of sodium hydroxide, — and to heat the solution until the excess of ammonium sulphide has been driven off, and the solution is again colorless. In this way there is formed either ammonium or sodium sulphocyanate, which, after acidifying, gives the characteristic blood-red color with ferric chloride.

Hydrogen cyanide may also be detected by the methods proposed by Kunz-Krause and by Schaer which have already been described under Cyanogen.

Determination of Hydrogen Cyanide.— For the determination of hydrogen cyanide in a gas mixture the method of L. W. Andrews¹ may be used. The gas is absorbed in potassium hy-

¹ *American Chemical Journal*, 30 (1903), 187.

dioxide and if the resulting solution contains more than about one per cent of hydrogen cyanide, it is diluted with water until its concentration does not exceed one per cent. Two drops of a saturated solution of pure paranitrophenol are then added. If the solution takes on a yellow color, decinormal hydrochloric acid is added until the color has very nearly disappeared. On the other hand, if the solution remains colorless, a decinormal solution of potassium hydroxide is added until a very pale-yellow tint is observed. 15 to 20 cc. of a solution of mercuric chloride containing 40 grams of the pure recrystallized salt to the liter is then added, and the solution is stirred and is allowed to stand for one hour at the temperature of the air. The hydrochloric acid set free in the reaction



is then titrated with a decinormal solution of potassium hydroxide, the end point of the titration being shown by the appearance of a pale-yellow tint in the solution.

HYDROGEN SULPHIDE (H_2S)

Properties of Hydrogen Sulphide. — Specific gravity, 1.1773; weight of one liter, 1.5230 grams.

According to Bunsen's experiments, water absorbs: —

at	2°	C.,	4.2373	vol. H_2S
"	9.8°	C.,	3.5446	" "
"	14.6°	C.,	3.2651	" "
"	19°	C.,	2.9050	" "

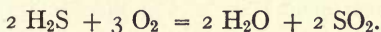
Between 2° and 43.3° the absorption by one volume of water at t°

$$= 4.3706 - 0.083687 t + 0.0005213 t^2 \text{ volumes of } \text{H}_2\text{S}.$$

According to the same authority alcohol takes up, between 1° and 22°, at temperature t ,

$$17.891 - 0.65598 t + 0.00661 t^2 \text{ volumes.}$$

One and a half volumes of oxygen are necessary for the combustion of one volume of hydrogen sulphide, and one volume of sulphur dioxide is formed.



Potassium hydroxide and solutions of salts of several other metals absorb hydrogen sulphide with the formation of a sulphide of the metals.

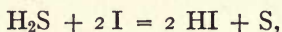
Detection of Hydrogen Sulphide. — If hydrogen sulphide is present in any considerable amount, its presence is disclosed by its odor. It may more certainly be detected by introducing into the gas a strip of moistened "lead-paper." Lead-paper is made by dipping filter paper into a solution of lead acetate, drying it and cutting it into narrow strips. In using it for testing for hydrogen sulphide it should first be moistened either with water or with dilute ammonium hydroxide. If hydrogen sulphide is present in the gas mixture, the paper becomes covered with a glistening brownish black layer of lead sulphide.

Another method for the detection of hydrogen sulphide is that devised by Ganassini.¹ It is based upon the fact that when ammonium molybdate is reduced by hydrogen sulphide, the molybdenum salt will react with potassium sulphocyanate to form molybdenum sulphocyanate which when dissolved in water yields a solution of pinkish red color. The reagent is prepared by dissolving 1.25 grams of ammonium molybdate in 50 cc. of water and 2.5 grams of potassium sulphocyanate in 45 cc. of water, mixing these two solutions and acidifying with 5 cc. of concentrated hydrochloric acid. The solution is said to be stable for some days if kept in a stoppered bottle and protected from the light. To test for the presence of hydrogen sulphide in the gas mixture the inside of a small porcelain evaporator is moistened with the reagent, and the gas under examination is caused to impinge upon the moistened surface. The test may also be made by dipping a piece of filter paper into the reagent and holding the moistened

¹ *Boll. Chim. Farm.*, 41 (1902), 417.

paper in the gas. If hydrogen sulphide is present, the liquid or the paper takes on a color that varies from a pale pink to a deep pinkish red according to the amount of hydrogen sulphide in the gas. Neither acetylene nor sulphur dioxide produces the red coloration.

Determination of Hydrogen Sulphide.—Hydrogen sulphide may quantitatively be determined by Dupasquier's method, a measured quantity of gas being drawn through a solution of iodine in potassium iodide, to which some starch paste has been added. The operation is stopped as soon as the solution becomes colorless. The reaction is —



but the reaction follows this equation precisely only when the solutions are very dilute and are protected from direct sunlight

R. Fresenius¹ determines hydrogen sulphide gravimetrically by first drying the gases with calcium chloride and then absorbing the hydrogen sulphide in U-tubes which are filled $\frac{5}{6}$ with pumice-stone impregnated with copper sulphate, and $\frac{1}{6}$, at the exit end, with calcium chloride. The pumice-stone is prepared as follows: Place 60 grams of pumice-stone, in pieces the size of a pea, in a small porcelain dish, and pour a hot concentrated solution of from 30 to 35 grams of copper sulphate over it. Evaporate the solution to dryness with constant stirring, place the dish in an air- or oil-bath, whose temperature is kept between 150° and 160° C., and let it remain there four hours.

A tube containing 14 grams of this copper sulphate pumice-stone takes up about 2 grams of hydrogen sulphide. To make sure of complete absorption two such tubes should always be used. When the pumice-stone is less thoroughly dried, it takes up a much smaller amount of hydrogen sulphide, and when it has been dried at a higher heat — until the copper sulphate has

¹ R. Fresenius, *Anleitung zur quant. Analyse*, 6th ed., Part I, p. 505. Also *Zeitschr. f. analyt. Chemie*, 10 (1871), 75.

lost its water of crystallization — it causes decomposition of the hydrogen sulphide and evolution of sulphur dioxide.

SULPHUR DIOXIDE (SO_2)

Properties of Sulphur Dioxide. — Specific gravity, 2.2131; weight of one liter, 2.8611 grams.

Sulphur dioxide is easily soluble in water. According to Sims, 1 volume of water dissolves at 760 mm. pressure —

at 7° ,	61.65 vol. SO_2		
“ 20° ,	36.43	“	“
“ 39.8° ,	20.5	“	“
“ 50° ,	15.62	“	“

One volume of water absorbs at 760 mm. pressure, and at temperatures between 0° and 20° , at t° ,

$$79.789 - 2.6077 t + 0.029349 t^2$$

volumes of sulphur dioxide; and 1 volume of the saturated aqueous solution contains, at t° ,

$$68.861 - 1.87025 t + 0.01225 t^2$$

volumes of the acid.

For temperatures between 21° and 40° , the coefficient of absorption is —

$$75.182 - 2.1716 t + 0.01903 t^2,$$

and the amount of gas contained by the saturated aqueous solution is —

$$60.952 - 1.38898 t + 0.00726 t^2 \text{ volumes.}$$

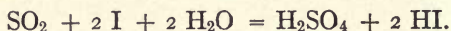
One volume of alcohol absorbs at 760 mm. pressure and t° , $328.62 - 16.95 t + 0.3119 t^2$ volumes of sulphur dioxide.

The alcoholic solution of sulphur dioxide, saturated at 0° , contains 216.4 volumes of the gas.

The gas reddens moist blue litmus paper.

The gas is readily absorbed by solutions of the hydroxides of the alkali metals.

Determination of Sulphur Dioxide. — Sulphur dioxide is determined either by leading a measured volume of the gas through a solution of bromine in water, and precipitating the sulphuric acid thus formed by barium chloride, or by measuring the amount of gas required to decolorize an iodine solution of known strength,



This latter method is very generally employed for the determination of sulphur dioxide in "burner gas," the usual procedure being that recommended by Reich.¹ The operation may be carried out in the apparatus shown in Fig. 25. *A* is a Friedrich's spiral gas washing bottle, *B* is a glass bottle of about three liters capacity and *C* is a 250 cc. graduated cylinder. 10 cc. of a standard solution of iodine containing 12.692 grams of iodine to the liter is poured into *A*. 65 cc. of water is then added together with sufficient of a starch solution to give to the liquid an intense blue color. *B* is filled nearly to the top with water and the siphon tube *D* is filled with water by applying suction at its lower end. The apparatus is then connected as shown in the figure and the inlet tube of *A* is joined by glass tubing to the chamber or pipe from which the gas is to be drawn. The screw pinchcock *E* is now opened and water is allowed to run out of *B* until a gas bubble starts to rise in the absorption bottle *A*. The graduated cylinder is then placed under the end of *D* and the water that flows from *B* is collected in it. In this manner the gas is slowly aspirated through the iodine solution until the liquid is decolorized. The pinchcock *E* is then at once closed and the volume of water that has collected in the graduated cylinder is measured.

The amount of sulphur dioxide in the mixture under examina-

¹ F. Reich, *Berg-und Hüttenmänn. Zeitung*, 1858.

tion may then be calculated as follows: One cc. of the standard iodine solution corresponds to 0.0032 gram SO_2 which amount under standard conditions possesses a volume of 1.118 cc. If b equals the prevailing barometric pressure, t the temperature, h the difference in height in millimeters between the level of the water in B and the lower end of the siphon tube D , and n the cubic centimeters of iodine solution employed, then the actual volume under the prevailing conditions of the sulphur dioxide, s , that has passed through the iodine solution may be calculated by use of the following formula:

$$s = 1.118 \times n \times \frac{760}{b - \frac{h}{13.6}} \times (1 + 0.00367 t) \text{ cc.}$$

The volume of the water, w , in the graduated cylinder C is equal to the amount of gas that has been drawn through A exclusive of the volume of sulphur dioxide; consequently the total volume of gas drawn into A equals $w + s$ and the per cent

of sulphur dioxide in the gas mixture equals $\frac{100 \times s}{w + s}$

If it should not be deemed necessary to introduce corrections for the pressure and temperature, the formula becomes

$$\frac{111.8 \times n}{w + 1.118 \times n} = \text{per cent } \text{SO}_2.$$

If 10 cubic centimeters of the standard (decinormal) iodine solution is used, the volume percentage of sulphur dioxide in the original gas mixture that is indicated by different volumes of water collected in the graduated cylinder is shown in the table on page 276.¹

An apparatus that is based upon the same principle as that of Reich, but which is so constructed that the per cent of sul-

¹ Lunge, *Sulphuric and Alkali*, 1903, vol. 1, part 1, p. 415.

CUBIC CENTIMETERS WATER COLLECTED	VOLUME PER CENT SO ₂ IN KILN GAS
82	12
86	11.5
90	11
95	10.5
100	10
106	9.5
113	9
120	8.5
128	8
138	7.5
148	7
160	6.5
175	6
192	5.5
212	5

sulphur dioxide in the gas mixture may be directly read off, has been described by Kreidl.¹

Determination of Sulphur Dioxide in presence of Nitrous Acid. — The method of Reich cannot be used for the determination of sulphur dioxide in the gases from the lead chambers of the sulphuric acid process because the hydriodic acid that is formed is quickly oxidized again to iodine by the nitrous acid that is present. The iodine that is thus set free then oxidizes additional amounts of sulphur dioxide with the result that the percentage of sulphur dioxide in the gas mixture appears to be much smaller than it actually is. Moreover, the presence of nitrous acid renders the end point of the reaction, the decolorization of the iodine solution, uncertain for the reason that after decolorization has been effected by the sulphur dioxide the blue color reappears because of the action of the nitrous acid. For the determination of sulphur dioxide in the presence of nitrous acid, it is consequently necessary to modify the method in such manner as to prevent the interference of nitrous acid and this is accomplished by Raschig² by adding sodium acetate to the solution. This

¹ *Z. f. Zuck.-Ind. Böhm.*, 24 (1900), 658.

² *Z. f. angewandte Chem.*, 22 (1909), 1182.

reacts with the free nitrous acid to form sodium nitrite and with the sulphur dioxide to form sodium sulphite, and these two salts do not act upon each other.

In the Raschig method the absorption bottle *A*, Fig. 25, contains 10 cc. of decinormal iodine solution, about 60 cc. of water, a little starch solution and 10 cc. of a cold saturated solution of sodium acetate. A U-tube or bulb tube containing cotton is placed between *A* and the lead chambers to prevent sulphuric acid from passing into the iodine solution. The amount of sulphur dioxide in the gas mixture is determined in the manner already described under the Reich method. The nitrous acid in the gases may then be determined by rinsing out the contents of the absorption bottle *A* into a flask, adding a drop of phenolphthalein, and titrating the free acetic acid with a decinormal solution of sodium hydroxide. From the volume of the sodium hydroxide solution used, there is to be subtracted 10 cc. for the hydriodic acid resulting from the reduction of the 10 cc. of decinormal iodine solution, and also 10 cc. more for the sulphuric acid formed in the reaction (see page 274). The balance of the sodium hydroxide that is used indicates free nitric acid or nitrous acid. Raschig states that while the method gives satisfactory results for sulphur dioxide, it is not very exact for the determination of the oxides of nitrogen if the gas sample is taken from the beginning of the lead chambers, because here the sulphur dioxide is present in preponderating amount. If, however, the gas sample is taken from the end of the chamber system where the oxides of nitrogen are present in much larger proportion, a proportionately larger sample of the gases will be needed to decolorize the iodine solution and a determination of the oxides of nitrogen will be correspondingly more exact.

CARBON OXYSULPHIDE (COS)

Properties of Carbon Oxysulphide. — Specific gravity, 2.0749; weight of one liter, 2.6825 grams.

Pure carbon oxysulphide has no odor, and its freshly prepared

solution in water has no taste. Its action upon the nervous system is somewhat similar to that of nitrous oxide.¹ When inhaled for a few seconds it causes dizziness and buzzing in the ears, but if the inhalation is not continued, the symptoms quickly disappear.

Water absorbs about one-third ² of its own volume of the gas.

A solution of potassium hydroxide absorbs carbon oxysulphide very slowly, but the gas is rapidly taken up by a solution prepared by dissolving one part of potassium hydroxide in two parts of water and adding an equal volume of alcohol. The analytical absorbing power of this solution is 18; that is, a cubic centimeter of this reagent is able to absorb 72 cc. of carbon oxysulphide. The gas is but slightly soluble in a hydrochloric acid solution of cuprous chloride. 1 cc. of this solution absorbs about 0.2 cc. of the gas.

Experiments made by Hempel ³ upon the analytical absorbing power of various reagents for carbon oxysulphide, hydrogen sulphide, and carbon bisulphide gave the following results:

REAGENT EMPLOYED	ANALYTICAL ABSORBING POWER		
	Carbon Oxysulphide	Hydrogen Sulphide	Carbon Bisulphide
Chloroform	—	—	2-3
Mixture { 1 part triethylphosphine	—	—	16
{ 9 parts chloroform			
Pyridine	1.1	4-5	9
Mixture { 1 part triethylphosphine	3	26	26
{ 9 parts pyridine			
{ 10 parts nitrobenzene	3	2	46
Nitrobenzene			
1 part potassium hydroxide in 2 parts water. One-half saturated with H ₂ S, and the 2 portions then mixed	—	—	1
Saturated solution of copper sulphate in a mixture of 200 grams water and 200 grams concentrated sulphuric acid	—	2.2	—

¹ Klason, *J. prakt. Chem.* 36 (1887), 64.

² Witzeck, *J. Gasbeleuchtung*, 46 (1903), 145.

³ *Z. f. angewandte Chem.* 1901, 865.

Carbon oxysulphide may be separated from hydrogen sulphide by absorbing the latter in an acidulated solution of copper sulphate (see table above). Separation from vapor of carbon bisulphide may be effected by passing the gases through a mixture of one part of triethylphosphine and nine parts of chloroform, which absorbs the carbon bisulphide. The most delicate reagent for its detection is iodide of starch. If the gas is passed through a starch solution that is colored a clear blue by a trace of iodine, the color of the solution is very slowly discharged. The blue tint changes first to violet, then to red, and finally the color disappears completely. Other gases that would act upon the iodide of starch must of course be absent.

One volume of carbon oxysulphide needs $1\frac{1}{2}$ volumes of oxygen for its combustion and yields one volume of CO_2 and one volume of SO_2 .

Determination of Carbon Oxysulphide. — Hempel determines ¹ carbon oxsulphide in the presence of hydrogen sulphide and carbon dioxide by first absorbing the hydrogen sulphide with an acid solution of copper sulphate, then decomposing the carbon oxysulphide into carbon monoxide and sulphur by passing the residual gas mixture through a hot capillary tube of platinum, determining the carbon monoxide that is here set free by absorption in a hydrochloric acid solution of cuprous chloride, and finally determining the carbon dioxide by means of potassium hydroxide.

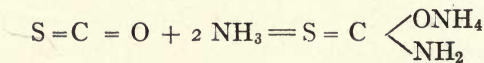
Witzcek ² raises objections to this method and gives preference to the procedure proposed by Lunge, which consists in passing the gas mixture through an iodine solution for the removal and the determination of hydrogen sulphide, and then shaking the residual gas with a solution of potassium hydroxide which will decompose the carbon oxysulphide with the formation of potassium sulphide and potassium carbonate. To this solution hydrochloric acid is then added to set free hydrogen

¹ *Z. f. angewandte Chem.* 1901, 865.

² *Loc. cit.*

sulphide and carbon dioxide. The hydrogen sulphide is determined by means of an iodine solution and the carbon dioxide is determined by absorption with potassium hydroxide. Since one volume of carbon oxysulphide yields upon decomposition one volume of hydrogen sulphide and one volume of carbon dioxide, the amount of carbon dioxide present in the original mixture is ascertained by subtracting from the volume of carbon dioxide formed, a volume equal to that of the hydrogen sulphide found to be present.

Carbon oxysulphide cannot be present in washed illuminating gas because as Witzeck points out it will be completely decomposed by the water vapor with which it comes in contact. Even if it should partially escape decomposition by water it would react very rapidly with ammonia or with ammonium hydroxide to form ammonium thiocarbamate,



FLUORINE (F₂)

Determination of Fluorine. — O. W. F. Oettel devised a method for the determination of fluorine in a substance, the fluorine being evolved as silicon tetrafluoride, and the volume of this gas then being directly measured. Since a large number of substances contain both fluorine and carbon dioxide, Hempel and W. Scheffler¹ have modified the method to permit of the simultaneous determination of fluorine and carbon dioxide in a single sample.

The fluorine is set free as silicon tetrafluoride together with carbon dioxide in a suitable apparatus, is collected in a burette, and the silicon tetrafluoride is then decomposed and absorbed by means of water (a small volume of carbon dioxide is here taken up by the water). The carbon dioxide still present in the gas is then completely removed by passing the gas into a pipette containing caustic potash. The gas residue is again brought

¹ *Z. f. anorg. Chem.*, 20 (1899), 1.

over the water which was first used and by which the silicon tetrafluoride was absorbed; the absorbed carbon dioxide hereupon escapes from the water and passes into the gas residue. Upon transferring the gas once more to the caustic potash pipette, the remainder of the carbon dioxide is removed, and this volume is subtracted from the diminution first obtained by the absorption with water. The difference gives the amount of silicon tetrafluoride. In this manner it is possible to make very sharp determinations of fluorine in the presence of carbon dioxide.

For setting free the silicon tetrafluoride there is used the apparatus shown in Fig. 87, II. The evolution flask is connected with a simple gas burette filled with mercury and containing on top of the mercury some concentrated sulphuric acid. It is well to join to the burette a level-bulb instead of a level-tube, and to attach a glass stopcock to the lower end of the burette tube (see Fig. 87).

The substance under examination is mixed with finely powdered quartz, the weight of the quartz being fifteen times that of the fluorine which is probably present in the material. The quartz is first heated for a long time in a muffle furnace with free access of air to remove every trace of organic matter.

The sulphuric acid to be employed must be freed from organic substances and from oxides of nitrogen. This is accomplished by adding to concentrated sulphuric acid about 5 grams of powdered sulphur and then fuming down the acid to two-thirds of its original volume.

In carrying out a determination the evolution flask II is first carefully dried and the substance, together with the proper amount of quartz powder, is then introduced into the flask by means of a long weighing tube, and the two powders are mixed as intimately as possible by shaking the flask. The flask is then joined by means of the capillary *d* and a piece of dry rubber tubing to the gas burette I which contains mercury and some sulphuric acid, as above described. The rubber tube is held

firmly in place by means of ligatures of light wire. The volume of concentrated sulphuric acid which is placed in the burette amounts to only about 0.25 cc. Its presence is necessary to avoid the possibility of decomposition of the silicon tetrafluoride by any moisture that might be in the burette.

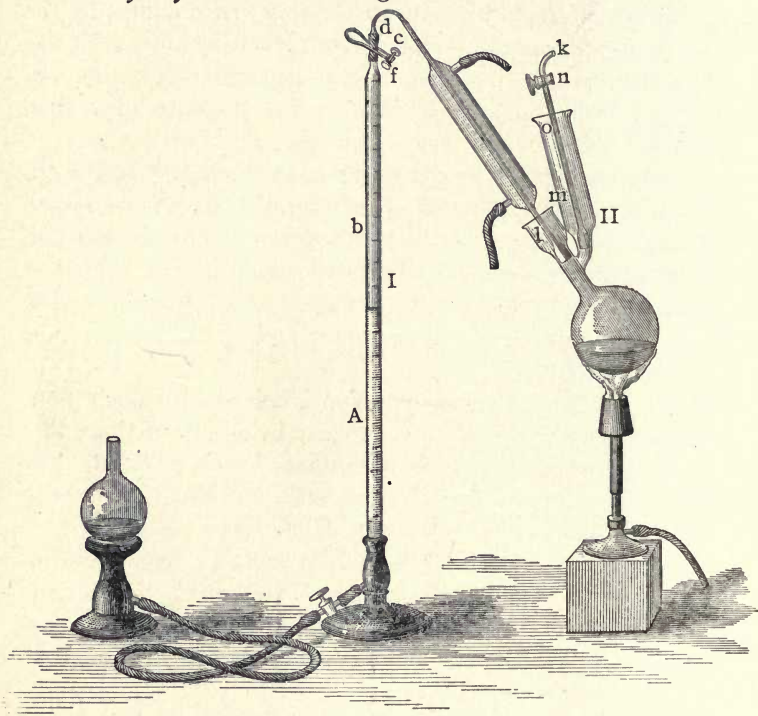


FIG. 87

In the bells *l* and *m* is placed some of the highly concentrated sulphuric acid. A water suction pump is now connected to *k*, and the flask II is partially exhausted. The stopcock *n* is then closed, and upon lifting the tube *o* sulphuric acid flows down from *m* into the flask. The flask is shaken so as to bring the acid into intimate contact with the mixture of quartz and the

substance, and the contents of the flask is then heated fully up to the boiling-point of sulphuric acid, the heating being continued for about fifteen minutes.

If the apparatus should break, the operator might be seriously injured by the hot concentrated sulphuric acid. It is well, therefore, to protect the eyes with goggles, and to place a glass screen between the flask and the operator.

The heating is now stopped, and the gas in the flask is completely driven over into the burette by filling *m* with concentrated sulphuric acid and carefully lifting the tube *o*. The flask is then disconnected from the burette and the total volume of the gas is measured.

The burette is now connected in the ordinary manner, by means of a capillary tube, with a simple mercury absorption pipette of the form shown in Fig. 88, the pipette containing 5 cc. of water above the mercury. The gas is transferred to the pipette and shaken for five minutes with the water. It is then brought

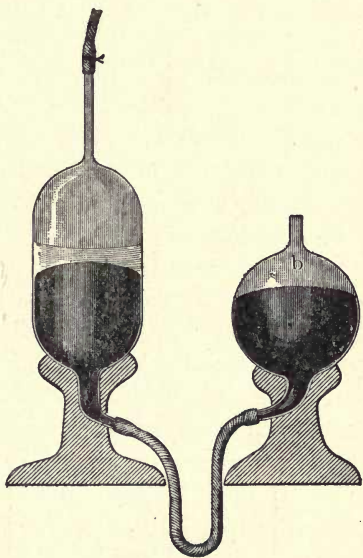


FIG. 88

back into the burette and the diminution in volume is read off.

The remaining gas is passed into a pipette filled with a solution of potassium hydroxide to absorb carbon dioxide, and is then drawn back into the gas burette. The volume is observed, and the gas is now passed into the first pipette, Fig. 88, and shaken again for three minutes. It is then passed back into the burette, and the residual volume of gas is measured. This gas is then passed once more into the potassium hydroxide

pipette to determine the small amount of carbon dioxide which was taken up by the water used in the first absorption of the silicon tetrafluoride.

All of these operations can be carried out with considerable speed, and it is therefore easily possible to make a determination of fluorine in two hours.

As an example of the accuracy of the method, the following result may be cited: 2.156 grams of the substance gave 3.56 cc. of silicon tetrafluoride, while theory called for 3.45 cc.

To illustrate the application of the method to the analysis of teeth, a few results of determinations of fluorine in teeth ash are tabulated below.

The incineration of teeth is easily effected in a hard glass tube in a current of oxygen if the powder is very fine and is placed in the tube in a very thin layer.

In determining fluorine in material that contains organic matter, it is very important that the substance should be completely incinerated, since the slightest trace of residual carbon would act upon the boiling sulphuric acid and cause the formation of sulphur dioxide, a gas which would then be absorbed by water when the silicon tetrafluoride is determined.

HUMAN TEETH	Grams of Teeth Ash taken	SiF ₄ + CO ₂ found	CO ₂	CO ₂ which was taken up by the water	SiF ₄ in cubic centi- meters	Fluorine in Grams	Per cent of Fluorine in the Teeth Ash
Unsound	1.793	1.0	4.65	...	1.0	0.0034	0.19
Sound	1.434	1.5	5.80	0.1	1.4	0.0047	0.33
Sound	0.831	1.6	3.50	...	1.6	0.0054	0.52

CHLORINE (Cl₂)

Properties of Chlorine. — Specific gravity, 2.4494; weight of one liter, 3.166 grams.

Chlorine is quite soluble in water. One part of cold water

dissolves approximately two volumes of chlorine; hot water dissolves less. According to Schönfeld, one volume of water absorbs the following volumes of chlorine: —

10°, 2.5852

15°, 2.3681

20°, 2.1565

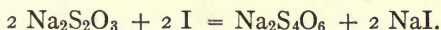
25°, 1.9504

30°, 1.7499

35°, 1.5550

40°, 1.3656.

Determination of Chlorine. — Chlorine may be determined by the Bunsen procedure, in which the gas is led through a solution of potassium iodide, and the iodine set free is titrated with sodium thiosulphate: —



Chlorine is absorbed by potassium hydroxide or sodium hydroxide. In cold dilute solutions the hypochlorite and chloride of the alkali are formed: —



In hot concentrated solutions, the reaction is: —



The first of these two reactions was used by Treadwell in the determination of chlorine in the presence of carbon dioxide, but Offerhaus ¹ found that even with a very dilute solution of sodium hydroxide an appreciable amount of sodium chlorate is formed, and that for this reason the titration of the hypochlorite with $\frac{\text{N}}{10}$ arsenious acid gives results about 0.7 per cent too low.

¹ *Z. f. angewandte Chem.*, 16 (1903), 1033.

Offerhaus obtained very satisfactory results by passing the mixture of chlorine and carbon dioxide through two dry Bunte burettes connected in series, determining chlorine in the first burette by absorbing the gas with a solution of potassium iodide and titrating the liberated iodine, and in the second burette determining the total amount of chlorine and carbon dioxide by absorption of the two gases with $\frac{N}{5}$ sodium hydroxide. The difference between the two results gives the amount of carbon dioxide.

To avoid the use of two gas burettes, Treadwell and Christie¹ absorb the chlorine in a decinormal solution of primary potassium arsenite, KH_2AsO_3 , and directly afterward determine the carbon dioxide in the gas mixture by absorption with a solution of potassium hydroxide.

They used a water-jacketed Bunte burette with a tail-stopcock at *G* (see Fig. 43) as well as at *C*, and with the upper part of the burette narrow to render more accurate the reading of small residual gas volumes. The burette is cleaned and thoroughly dried, and the gas mixture is then passed into the burette through the end of the lower stopcock and out through the upper stopcock, the passage of the gas being continued until all of the air that was originally in the burette has been displaced. The lower stopcock is then closed and after ten seconds the upper stopcock is closed and the barometric pressure and temperature of the water surrounding the burette are noted. The lower stopcock is then turned so that the upper end of the stopcock communicates with the tube *H* from the level-bottle *B*. Treadwell and Christie use a level-tube in place of the level-bottle. The level-tube is filled with distilled water and this is allowed to flow through the rubber tube *H* and out through the end of the lower stopcock *G* to expel air from the tube and chlorine from the end tube and lower stopcock. When the water has flowed out of the level-tube and only the connecting rubber tube *H* is

¹ *Z. f. angewandte Chem.*, **18** (1905), 1930.

filled with water, the stopcock *G* is closed and there is poured into the level-tube exactly 100 cc. of a decinormal solution of primary potassium arsenite. This solution is prepared by dissolving 4.95 grams of arsenic trioxide in a dilute solution of potassium hydroxide, adding phenolphthalein and then sulphuric acid until the color of the solution disappears, and finally diluting to one liter. The lower stopcock is then turned so that the level-tube communicates with the burette. The arsenite solution at first rises rather slowly in the burette, but later its passage is more rapid. Toward the close of the absorption of the chlorine, the burette is shaken to hasten the completion of the reaction.

After the absorption of the chlorine has been effected, which takes about 5 minutes, the liquid in the two tubes is brought to the same height and the volume of gas remaining in the burette is read off. The level-tube is now lowered, 10 cc. of a solution of potassium hydroxide (1:2) is poured into the funnel *D*, the upper stopcock *C* is carefully opened and the solution drawn down into the burette. The stopcock is then closed, the burette is shaken to hasten the absorption of the carbon dioxide, the liquid in the burette and level-tube is brought to the same height and the residual gas volume is read off the temperature and barometric pressure being again noted.

All of the liquid in the level-tube and in the burette is then transferred to an Erlenmeyer flask and the apparatus thoroughly rinsed with water which is also added to the contents of the flask. Some phenolphthalein is then added to the solution and dilute hydrochloric acid (1:4) is run in until the red color of the liquid just disappears. 60 cc. of a solution of sodium bicarbonate containing 40 grams of the salt to the liter is then added together with a little starch solution, and the excess of arsenious acid is determined by titration with $\frac{N}{10}$ solution of iodine.

In calculating the results, allowance must be made for the fact that the original mixture of chlorine and carbon dioxide is

usually practically free from moisture, while the gas residue in the burette is measured in the moist condition. The volume which the residual gas would occupy if dry and at the pressure and temperature under which the gas sample was measured must consequently first be calculated. The difference between this volume and the original volume of the sample in the burette will give the total amount of chlorine and carbon dioxide. The amount of chlorine may be read off after the absorption of that gas by the arsenite solution and the correction of the residual volume, or it may be determined by titration with an iodine solution as above mentioned. One cc. of an $\frac{N}{10}$ solution of iodine corresponds to 0.003546 gram chlorine, and this weight of chlorine under standard conditions will occupy a volume of 1.1015 cc.

Treadwell and Christie state that the determination of chlorine by absorption with the arsenite solution agrees quite closely with the results obtained by titration, the average difference amounting to 0.13 per cent.

If a solution contains free chlorine together with hydrochloric acid, they may both be determined in the following manner (Fresenius): —

To a weighed portion of the liquid add an aqueous solution of sulphurous acid until the latter is in excess; after some time add nitric acid and then some potassium chromate to destroy the excess of sulphur dioxide, and precipitate the total chlorine as silver chloride.

If now the amount of free chlorine is determined in a second portion by potassium iodide, the difference gives the quantity of chlorine present in the form of chloride.

The total chlorine may be volumetrically determined by absorbing the gases with a solution of sodium hydroxide, adding sulphur dioxide, then, after a while, nitric acid and some potassium chromate, and finally neutralizing the solution by adding calcium carbonate. All chlorine is now present as chloride, and

the solution is neutral, so that the chlorine may be titrated with a neutral silver solution, potassium chromate being used as indicator.

HYDROGEN CHLORIDE (HCl)

Properties of Hydrogen Chloride.—Specific gravity, 1.2595; weight of one liter, 1.6283 grams.

According to Roscoe and Dittmar, one volume of water dissolves at 0°, 503 volumes of hydrogen chloride. The parts by weight of the gas which dissolve in one gram of water at a pressure of 760 mm. and at different temperatures, are given in the following table:—

TEMPERATURE	HCl	TEMPERATURE	HCl
0	0.825	32	0.665
4	0.804	36	0.649
8	0.783	40	0.633
12	0.762	44	0.618
16	0.742	48	0.603
20	0.721	52	0.589
24	0.700	56	0.575
28	0.682	60	0.561

At ordinary temperatures, one volume of alcohol dissolves 327 volumes of hydrogen chloride.

Determination of Hydrogen Chloride.— If no other acid gas is present with the hydrogen chloride, it may be determined by drawing a measured quantity of the gas through a standardized solution of an alkali and titrating back with an acid.

Hydrogen chloride may also be determined by absorbing it with an alkaline solution free from chlorine, and, after acidifying, precipitating it with silver nitrate, and weighing as silver chloride.

A method proposed by Cl. Winkler,¹ and based upon J. Volhard's volumetric method for the determination of silver,² con-

¹ Cl. Winkler, *Anleitung zur Untersuchung der Industrie-Gase*, Part II, p. 322.

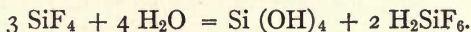
² J. Volhard, *Zeitschrift für analyt. Chemie*, 13 (1874), 171, and 17 (1878), 482.

sists in placing in a suitable absorption apparatus a few drops of ammonium sulphocyanate or potassium sulphocyanate, some iron alum solution, and a measured amount of $\frac{N}{10}$ silver nitrate solution. Upon leading the gas through this solution the hydrochloric acid reacts with the silver, forming silver chloride. The end of the reaction is shown by the blood-red color. The appearance of this color is due to the fact that after all of the silver nitrate has been changed to silver chloride, the silver sulphocyanate present is also decomposed and ferric sulphocyanate is formed. The volume of the gas is measured and the amount of hydrogen chloride that it contains is calculated.

SILICON TETRAFLUORIDE (SiF_4)

Specific gravity, 3.60; weight of one liter, 4.663 grams.

The gas is completely absorbed by water, and is at the same time decomposed —



This reaction, which has been employed by R. Fresenius¹ for the quantitative determination of fluorine, might possibly be made use of for the determination of silicon tetrafluoride in gases.

PHOSPHINE (PH_3)

Properties of Phosphine. — Specific gravity, 1.175; weight of one liter, 1.52 grams.

Phosphine is a colorless gas with a very unpleasant odor resembling that of decayed fish. It is very poisonous. The pure gas takes fire only at a temperature above 100° . It can be mixed with pure oxygen without change, but if the mixture be suddenly brought under diminished pressure, it explodes. Phosphine takes fire when brought in contact with a drop of fuming nitric acid, or with chlorine or bromine.

¹ Fresenius, *Quant. chemische Analyse*, 6th ed., Part I, p. 431.

Phosphine is somewhat soluble in water. One volume of water absorbs about 0.02 volume of the gas, and takes on its odor and a disgusting taste. Exposed to the light, the solution decomposes with evolution of hydrogen and separation of amorphous phosphorus. The gas is decomposed by the electric spark into phosphorus and hydrogen.

When a strip of silver nitrate test paper is brought into contact with the gas, the paper is at once blackened, metallic silver and phosphoric acid being formed.

If phosphine is passed through a neutral aqueous solution of potassium mercuric iodide, a crystalline, orange-yellow precipitate, PHg_3I_3 , is produced.¹

Determination of Phosphine. — Phosphine may be determined by converting it into phosphoric acid either by burning it or by passing it through bromine water or a solution of sodium hypochlorite and precipitating the resulting phosphoric acid with magnesia mixture. These reactions may also be utilized for the detection of phosphine in a gas mixture, the phosphoric acid being identified by precipitation with ammonium molybdate.

Further details concerning the determination of phosphine, particularly in the presence of acetylene, are given on p. 360.

ARSINE (AsH_3)

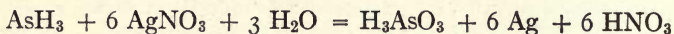
Properties of Arsine. — Specific gravity, 2.696; weight of one liter, 3.485 grams.

Arsine is a colorless gas of very unpleasant odor. It is extremely poisonous. When passed through a highly heated tube, the gas is decomposed and a glistening mirror of metallic arsenic is deposited. The gas is slightly soluble in water.

The best confining liquid for gas mixtures that may contain arsine is a freshly boiled concentrated solution of sodium chloride. Arsine is completely and rapidly absorbed by solutions of

¹ Lemoult, *Compt. rend.*, **139** (1904), 478.

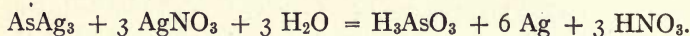
silver nitrate. The reaction with dilute neutral silver nitrate or with a slightly acid solution of this salt does not quantitatively proceed according to the Lassaigne¹ reaction



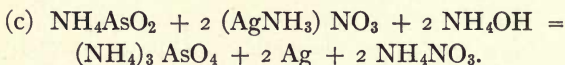
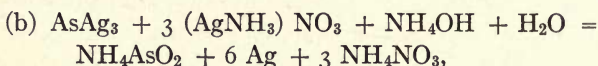
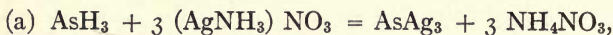
but in part follows the equation: —



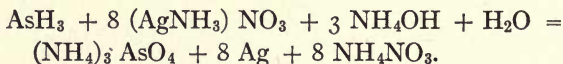
In the presence of an excess of silver nitrate the silver arsenide formed in the preceding reaction gradually undergoes change as follows:



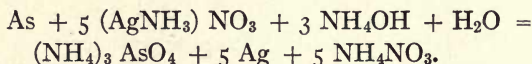
In dilute ammoniacal silver solution three reactions appear to occur:



If, however, the solution is heated for some time after absorption, the end reaction may be expressed by the equation:



When metallic arsenic stands in contact with an ammoniacal silver solution and the solution is warmed, the arsenic is oxidized to arsenic acid.²



¹ *J. chim. medic.*, 16 (1840), 685.

² Most of the above details are from the article by Reckleben, Lockemann and Eckardt, *Z. f. analyt. Chem.*, 46 (1907), 671.

Detection of Arsine. — Arsine may be detected by allowing the gas to act upon a crystal of silver nitrate. If the amount of arsine in the gas mixture under examination is not too great, there is formed a yellow compound which is said to be $\text{AsAg}_3 \cdot 3 \text{AgNO}_3$. If the gas contains considerable arsine, the yellow color appears only for an instant and changes to black almost immediately. If the gas mixture contains hydrogen sulphide, this is removed by passing the gases through a glass tube that contains first a plug of cotton, then a second plug of cotton that has been moistened with a solution of ammonium lead acetate, and beyond this a crystal of silver nitrate and one of lead acetate. The latter serves to show whether any hydrogen sulphide has passed the second cotton plug.

Arsine may also be detected ¹ by passing the gas into a rather concentrated ammoniacal silver solution which is at once darkened by the slightest traces of the gas. The test does not serve to detect arsine in the presence of stibine, phosphine, or hydrogen sulphide, because those gases also cause a darkening of the silver solution.

Determination of Arsine. — Arsine cannot accurately be determined by passing the gas into a solution of silver nitrate and ascertaining either the amount of silver precipitated or of arsenious acid formed.² It may, however, be volumetrically determined by absorbing the gas with a neutral solution of silver nitrate or with a solution of sodium hypochlorite containing three per cent of active chlorine.

STIBINE (SbH_3)

Specific gravity, 4.33; weight of one liter, 5.6 grams.

Stibine is a colorless gas of less pronounced odor than arsine. It is but slightly soluble in water.

When stibine is passed into a solution of silver nitrate a black precipitate, SbAg_3 , is formed. If this substance is washed with

¹ Reckleben and Lockemann, *Z. f. angew. Chem.*, 19 (1906), 275.

² Reckleben and Lockemann, *loc. cit.*

water and boiled with tartaric acid, it is decomposed with the formation of silver and a soluble compound of antimony.

When stibine acts upon a crystal of silver nitrate, the black compound, SbAg_3 , is formed.

Stibine may be determined by passing the gas into a solution of silver nitrate, collecting the silver antimonide on a filter, washing it, decomposing it with tartaric acid and determining the antimony in solution.

CHAPTER XIV

FLUE GAS ANALYSIS

In the examination of the efficiency of the various devices in which the chemical energy of the fuel is transformed into heat energy, it is usually necessary to determine the composition and the heating value of the fuel, and to make an analysis of the gas mixture that passes from the zone of combustion into the flue. The analysis of solid and liquid fuels does not fall within the scope of the present work, but the analysis of flue gas will here be considered, and the determination of the heating value of solid, liquid and gaseous fuel and the analysis of combustible gas mixtures will be discussed in later chapters.

When carbon is burned in air, one volume of oxygen unites with solid carbon to form one volume of carbon dioxide. If pure carbon could be completely burned with an amount of air that contains oxygen just sufficient for the conversion of the carbon to carbon dioxide, the escaping gases would contain the same amount of carbon dioxide as there is oxygen in the air, namely, about 21 per cent. The combustible matter in commercial fuels does not, however, consist entirely of pure carbon, and consequently the theoretical amount of carbon dioxide that would be formed in their complete combustion will always lie below 21 per cent. If the attempt should be made in actual practice to cut down the air supply to the amount theoretically needed for the combustion of the fuel, incomplete combustion would result. The amount of air admitted to the fuel is, in proper firing, from one and a half to two times that theoretically necessary, with the result that the percentage of carbon dioxide in the flue gas will range from about nine to fourteen per cent. With careless firing or faulty construction of the furnace the per cent

of carbon dioxide in the flue gas will fall below the above amount and the per cent of oxygen in the escaping gases will correspondingly rise. The greater the excess of air admitted to the furnace the larger will be the amount of heat carried off through the flue by the gases.

In the analysis of flue gas, it is at times sufficient to determine merely the carbon dioxide in the gas mixture. Usually, however, as in a boiler test, it is necessary to determine both carbon dioxide and oxygen (and also carbon monoxide if present, although this is rarely the case).

Sampling of Flue Gas. — If the operator wishes merely to ascertain the percentages of these three gases in the flue gases at certain intervals, the gases from the fire may be drawn by a bottle aspirator through a tube provided with a T-tube (see Fig. 7) to which a gas burette is attached in the manner shown. Any other aspirating device may of course be employed in place of the bottle aspirator. It is inadmissible to collect or store over water any gas mixture containing carbon dioxide if, in the determination of that gas, results of more than approximate accuracy are desired. The small bottle *E* contains a little water which serves to wash the flue gases and to indicate their speed of flow. Before a sample of the flue gases is drawn off in the Hempel burette, the pinchcocks *d* and *f* are opened and the level-tube is raised until the confining liquid stands at *c*. In drawing off the sample for analysis, *d* and *f* are opened and the level-tube is slowly lowered until slightly more than 100 cc. of gas has been drawn into the burette. The two pinchcocks are then closed and the rubber tube at the top of the burette is slipped off the lower end of the glass tube *e*. If only approximate results are required, water may be used as the confining liquid in the burette. For more accurate work mercury should be employed.

If an average sample of the flue gases covering a period of several hours is desired, the sampling tube of Huntly (see p. 5) should be employed and the sample collected over mercury.

Although Huntly gives no description of the method to be followed in transferring the gas from the sample tube to a Hempel gas burette, it is obvious that this may easily and accurately be done in the following manner:

Invert the tube and fasten it in a clamp. Connect a mercury level-bulb with the capillary tube *A* by a piece of rubber tubing about 40 cm. long. Turn the stopcock *H* so that *A* communicates with the side capillary tube *B*, thus driving all air out of *A*. Connect the capillary tube *F* with the capillary connecting tube of the burette by a short piece of rubber tubing in the usual manner, and turn the stopcock *K* so that *F* opens into *E*. Open the pinchcock of the burette, raise the level-tube and in this manner fill *F* with mercury. Upon now turning the stopcock *H* and *K* to such positions that *A* and *F* communicate with *C*, and lowering the level-tube of the burette, the gas sample will be drawn over into the burette without possibility of admixture with air.

Analysis of Flue Gas. — If the sample of flue gas is taken in the neighborhood of the laboratory, the analysis may rapidly and accurately be made either with the form of Orsat apparatus devised by the author and described on p. 85, or with the apparatus of Hempel. If the latter is used, a sample of 100 cc. is measured off in a Hempel burette in the manner described on p. 59. The three gases, carbon dioxide, oxygen and carbon monoxide, are then absorbed in the order given, the decrease of volume in cubic centimeters in each case giving directly the percentage of the constituent in the flue gas.

Carbon dioxide is absorbed in a Hempel simple gas pipette for solid reagents that is filled with a concentrated solution of potassium hydroxide (see p. 225). The pipette is connected with the burette in the manner that has already been described in detail on p. 61 and the complete removal of the carbon dioxide is accomplished by passing the gas mixture into the pipette, allowing it to remain there for a moment and then drawing it back into the burette. If water is being used as the con-

fining liquid in the burette, it is allowed to run down for one minute and the residual gas volume is then read off, the diminution in volume being equal to the per cent of carbon dioxide in the flue gas. For the removal of oxygen a pipette containing phosphorus (see p. 164), alkaline pyrogallol (see p. 160) or sodium hyposulphite (see p. 168) may be employed; the manipulation described under these various reagents should be carefully followed so that the complete removal of all of the oxygen in the gas mixture may be insured. In the analysis of flue gas with the older or, indeed, with some of the later modifications of the Orsat apparatus, oxygen is not entirely removed. Since this gas is absorbed by cuprous chloride which is next used for the determination of any carbon monoxide that may be present, a diminution in volume resulting from the absorption of oxygen by the cuprous chloride would naturally be ascribed to carbon monoxide in the gas mixture. This is a frequent cause of error in the analysis and in the calculations that are based upon it.

After the oxygen has been absorbed, a double gas pipette containing ammoniacal cuprous chloride (see p. 232) is connected with the burette, the residual gas is passed over into the pipette and the absorption of carbon monoxide is effected by gently shaking the pipette backward and forward without disconnecting it during a period of three minutes. There will usually be no diminution in volume after this treatment, for flue gas rarely contains carbon monoxide. It is true that many analyses show an appreciable amount of this constituent in the gases formed in combustion, but in the experience of the author, this is due in the great majority of cases to the incomplete removal of oxygen referred to in the preceding paragraph.

If the Orsat-Dennis apparatus is employed, the absorption pipette next to the burette is filled with a solution of potassium hydroxide, the next pipette with a solution of sodium hyposulphite or of alkaline pyrogallol and the third pipette with an ammoniacal solution of cuprous chloride. Carbon dioxide, oxygen and carbon monoxide are then absorbed by the three

reagents in the order given. The manipulation of the apparatus is described on p. 87.

Any sulphur dioxide that is present in the flue gas will be absorbed by potassium hydroxide in the determination of carbon dioxide. If it is desired to determine the amount of sulphur dioxide present, a fairly large sample of the gas should be drawn directly from the flue through a tube containing a wad of cotton to stop the dust, then through a gas washing bottle containing a measured volume of a standard iodine solution and finally through a gas meter for measurement. Full details of this method will be found on p. 274.

If the plant that is being tested is at a considerable distance from the laboratory, it is frequently more convenient to make the analysis of flue gas on the spot than to transport the gas sample to the laboratory. In such case the portable Hempel apparatus described on p. 69 or the Orsat-Dennis apparatus may be employed with equally good results.

Automatic Flue Gas Analysis. — The character and completeness of the combustion in a furnace or other heating apparatus may, to a considerable degree, be judged by the percentage of carbon dioxide in the gases escaping through the flue. This fact has led to the invention of a number of devices for automatically and continuously determining carbon dioxide.

Some of these instruments, those that are based upon the determination of the specific gravity of the flue gas, render it possible to read off the per cent of carbon dioxide at any time, but do not record the results. The gas balance of Lux, the dasymeter of Siegert and Dürr and the econometer of Arndt are instruments of this type. It is reported that they are no longer used in practice. The apparatus of Krell-Schultze which is based on this principle has met with favor in certain quarters.

The Carbon Dioxide Recorder. — Another form of apparatus is that in which carbon dioxide in the flue gas is absorbed, and the gas volume after the absorption is automatically recorded. As an example of instruments of this form the Pre-

the siphon tank that contains the float *b*; *dd* is the extractor tank and bell; *jj* is the recorder tank with counterbalanced bell. A small stream of water flows in constantly through *x* and enters the reservoir *k* which is provided with an overflow pipe *oo*. The water flows from the reservoir *k* into the siphon tank *a* through the hollow valve stem *e*. As the water enters *a* the float *b* is raised, and the bell *d*, which is connected with *b* by means of the chain *cc*, falls. When the float *b* rises to the top of the siphon tank it strikes the valve stem *e*, trips the valve and momentarily flushes the siphon tank, the water flowing out of *a* through the tube *g*. This causes the weighted float *b* to fall; as it does so it lifts the extractor bell *d* and thus draws into *d* through the pipe *p* and the three-way cock *h* a sample of flue gas.

The water that passes through the siphon tube *g* falls into the small pan below *g* which then drops, thereby raising the counterweight *q* and closing the valve *h*. This pan is automatically emptied in time to allow the valve *h* to open again after the proper interval.

In the meantime water has been flowing into the siphon tank *a* thus raising the float *b* and lowering the extractor bell *d*. As the bell sinks, the flue gas that it contains is gradually brought under pressure and is forced down through the pipe that connects with *d*, and through a solution of potassium hydroxide contained in the reservoir *m*. The carbon dioxide in the flue gas is here absorbed and the residual gas passes upward into the recorder tank *j* and raises the bell in that tank. Attached to the side of this bell *j* is a scale *n* that is graduated from 100 % at the bottom to zero per cent at the top. The capacity of the bell of the extractor tank *d* is so chosen that when air that is practically free from carbon dioxide is passed through the apparatus, the recorder bell *j* rises to the zero point on the scale. When flue gas is passed through the apparatus, the same volume of gas is collected in the bell *d*, but on passage through the solution of potassium hydroxide the carbon dioxide in this mixture is absorbed, with a consequent reduction in the volume of the gas

escaping into j . The height to which j rises, and consequently the percentage of carbon dioxide in the gas mixture is automatically recorded. The gas in j is then discharged into the outer air and the fresh sample of gas passes into it from m .

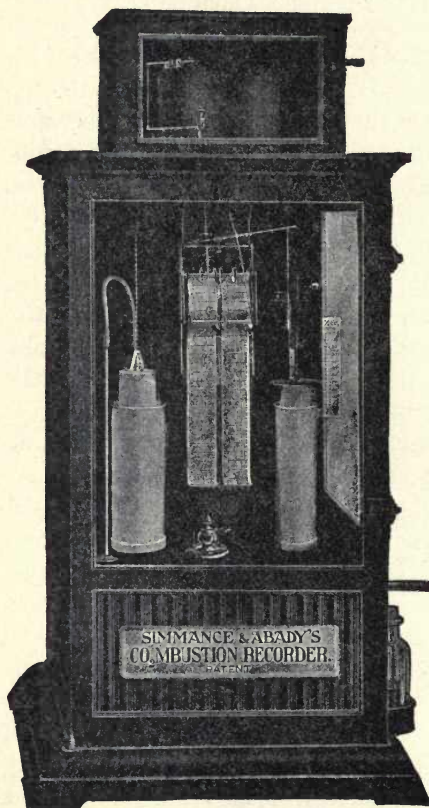


FIG. 90

To insure constant flow of fresh flue gas into the apparatus, the inlet water tube at x is caused to act as an injector or aspirator, and is connected with p by a branch pipe that rises and is joined to the aspirator by the side arm p_1 . This serves to continuously exhaust the pipes that connect the recorder to the boilers, which insures that the successive samples of gas that are analyzed are from the boiler flue and are not stagnant gases from the connecting pipes. Fig. 90 shows this recorder mounted and ready for use.

The Autolysator. —

Instruments of the above type are open to the objection that

the analyses are separated by intervals of several minutes, which renders it impossible to read the carbon dioxide content of the flue gas at any desired moment. This difficulty is

overcome by such an apparatus as the Autolysator of Strache, Johoda and Genzken.¹

This instrument renders it possible to read off, at any moment, the per cent of carbon dioxide then present in the flue gas, and it also furnishes a continuous record of the percentage of this gas. The essential parts of the device are shown in Fig. 91. *K* is a capillary tube the ends of which communicate with the differential manometer *M*. One end of *K* is connected with the regulating valve *A* which in turn is joined to a water suction pump.

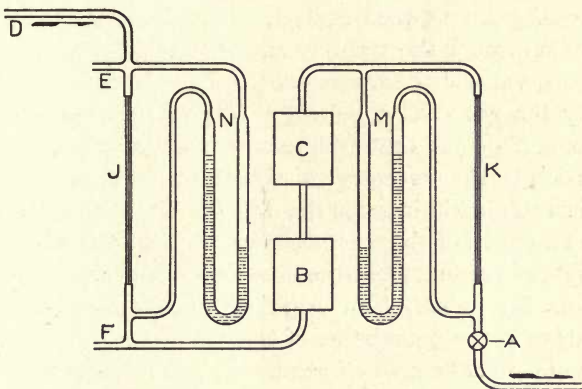


FIG. 91

The passage of the gas through the capillary *K* is dependent upon the difference in pressure shown upon the manometer *M*. If the volume of gas is kept constant by a proper adjustment of the valve *A* the volume of gas passing through *K* is also constant. The specific gravity of the gas has no influence upon the speed of flow through the long capillary tube. The constant volume of gas passing through *K* is drawn through a second capillary *J* the two ends of which are joined to the manometer *N*.

Between the two capillary tubes are introduced the absorption vessels *B* and *C* which serve to free the gas that is passed

¹ *Z. f. chemische Apparatenkunde*, 2 (1907), 57.

through *J* from the constituent that is to be determined. The gas mixture under examination enters the apparatus at *D*.

It is apparent that if no gas is absorbed when the mixture passes through *B* and *C* the same amount of gas will pass through the capillary *J* in a unit of time as flows through the capillary *K*. If the two capillaries are exactly the same diameter and length, the difference in pressure in *N* will be exactly the same as that shown by *M*. If, on the other hand, the absorption vessels *B* and *C* remove a constituent of the gas mixture, then a larger volume of gas must pass through the capillary *J* in a unit of time than through the capillary *K*. If, now, with the aid of the regulating valve *A* the reading of the manometer *M* and consequently the gas volume flowing through *K* be kept constant, the amount of gas that will pass through *J* will increase in proportion to the percentage of absorbable constituents that it contains. This will increase the difference in level of the liquid in the two arms of the manometer *N* and this difference shows directly the percentage of the absorbed constituent in the gas mixture. By means of an empirical scale attached to *N* the percentage in the gas mixture of the gas that is being absorbed in *B* and *C* may be read off at any moment. The apparatus is further provided with an automatic registering device which gives a continuous record of the percentage of absorbed gas. This form of autolysator is manufactured by the Vereinigte Fabriken für Laboratoriumsbedarf, Berlin.

The Gas Refractometer. — Another interesting instrument for the determination of a constituent gas in a mixture of gases is the Gas Refractometer designed by Haber.¹ The method is based upon the fact, first ascertained by Dulong,² that the light-refraction of gases may be determined with exactness by means of a gas prism and telescope; and upon the law of Biot and

¹ *Vortrag auf der Hauptversammlung des Vereins deutscher Chemiker, Nürnberg, June 8, 1906.* Also in *Zeit. f. angew. Chem.*, **19** (1906), 1418.

² *Ann. de chim. et de phys.*, **31** (1826), 154.

Arago¹ that the light-refraction of a gas mixture may be calculated in simple manner from the refraction of the several constituents and their partial pressures.

In other words, if the index of refraction, less one, is termed the refractive power, the total refractive power of a gas mixture is equal to the sum of the refractive powers of the constituent gases in the same manner as the total pressure of a gas mixture is equal to the sum of the partial pressures of the several gases that are present.

To determine the percentage of a gas in a mixture with the aid of the gas refractometer, the refraction of the mixture is first measured, and then the refraction of the residue after the removal of the constituent in question. Or if it is desired to ascertain the amount of a gas that has been added to a mixture, as in the carburetting of illuminating gas, the refraction before and after the addition of the gas is measured.

The refractometer has been successfully employed in the solution of certain special problems in technical practice. It is manufactured by the firm Carl Zeiss in Jena, Germany.

¹ *Mem. de l'Acad. de France*, 7 (1806), 301.

CHAPTER XV

ILLUMINATING GAS—FUEL GAS

COAL GAS—PINTSCH GAS—WATER GAS—PRODUCER GAS
BLAST-FURNACE GAS—NATURAL GAS

The gas mixtures that fall under the above heading show great differences in composition, but they are here grouped together because the methods employed for their analysis and the sequence of the several determinations are closely similar and, in many cases, identical.

Probably the most complex of these gas mixtures is that which results from the destructive distillation of coal, a product termed *coal gas*. A detailed description of the methods employed in the examination of this gas is given in the following pages, and will be found to include practically all of the points involved in the analysis of the other gas mixtures enumerated at the head of this chapter.

COAL GAS

Although the quantitative composition of coal gas varies with the methods employed in its manufacture and with the nature of the coal, the constituents of the product are nearly the same in every case. The washed gas contains carbon dioxide, carbon monoxide, hydrogen, methane, heavy hydrocarbons (illuminants), vapors of other hydrocarbons such as benzene and naphthalene, gaseous compounds of sulphur, water vapor, nitrogen, oxygen, and sometimes cyanogen or hydrogen cyanide. The unwashed gas contains ammonia and uncondensed tar, in addition to the above ingredients.

The complete examination of coal gas comprises:—

1. The determination of the illuminating power of the gas;

2. The determination of the specific gravity of the gas;
3. The gas volumetric determination of the principal constituents of the gas mixture;
4. The determination of naphthalene;
5. The determination of the total sulphur in the gas;
6. The determination of the total cyanogen in the gas;
7. The determination of the heating value of the gas (see Chapter XVI).

1. *The Determination of the Illuminating Power of Coal Gas*

In the measurement of the intensity of sources of light two general methods are employed, the direct-comparison method and the substitution method. In the first, the light whose intensity is to be measured is placed on one side of the photometric apparatus and the standard light on the other side and the two are directly compared. In the second, a light of convenient intensity is compared with the standard; the standard is then removed and the light whose intensity is to be compared is then put in its place. The intensity of the last light in the terms of the standard is then computed.

While the substitution method is in general superior to that of direct comparison the latter is usually employed in the industrial measurement of the illuminating power of gases.

The most satisfactory primary standards are the sperm candle, the pentane lamp, the Hefner amylacetate lamp and the carbon-filament incandescent lamp.¹ Many forms of photometer have been devised. Full details concerning their construction and use may be found in *Praktische Photometrie* by Dr. Emil Liebethal (1907) and in *Photometric Units and Standards* by E. B. Rosa (see note).

Of the direct comparison instruments, that designed by Bunsen is widely used and gives quite satisfactory results. The instru-

¹ A discussion of these standards will be found in the lecture of Rosa upon photometric units and standards published in *Lectures on Illuminating Engineering*, The Johns Hopkins Press, 1911.

ment is constructed on the following principle. If a spot upon a screen of white paper is rendered translucent by pressing grease or wax into the paper, and the screen is then held between two sources of light, the grease spot will appear darker than the surrounding paper when the screen is viewed from the side on which the stronger light falls. If the illumination on the further side of the paper is the stronger, the spot will appear to the eye to be lighter than the rest of the screen. If the screen is moved to such position between the two sources of light that the intensity of light falling upon each side of it is the same, the spot will disappear. The distance from the screen to each of the two lights is now measured. Since the intensities of the two flames are to each other as the squares of the distances of the flames from the screen, the candle power of one flame in terms of the other may be computed according to the formula

$$I' = I \frac{d'^2}{d^2}$$

in which I is the candle power of the light of known intensity

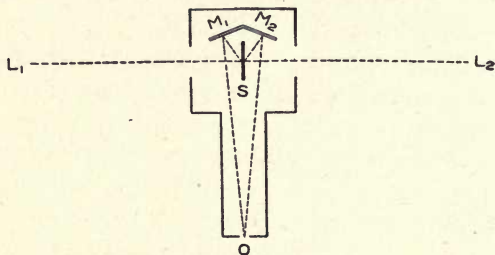


FIG. 92

and d the distance of this light from the screen, and I' is the candle power of the light being measured and d' its distance from the screen.

The construction of the Bunsen photometer is shown in Fig. 92.

L_1 and L_2 are the two sources of light under comparison and

S the screen of paper on which is the grease spot. To enable the operator to see both sides of the screen simultaneously, the Rüdorff mirrors M_1 and M_2 , each placed at an angle of 70° with the plane of the screen, are almost universally employed. Upon looking through the opening *O* the eye sees the two images of the disk.

In determining the intensity of a source of light L_2 , in terms of L_1 , the photometer screen is moved to the right or left until the contrast between the greased and ungreased portions of the screen is the same on one side as on the other. The distances from the screen to the two sources of light are then read off, and the intensity of L_2 computed by means of the formula given above.

2. The Determination of the Specific Gravity of Coal Gas

The specific gravity of coal gas is usually determined by measuring its time of escape through a small opening. Methods that may be employed for this purpose are described on p. 44.

3. The Gas-Volumetric Analysis of Coal Gas

The volumetric analysis of coal gas comprises the determination of such constituents as are present in amounts sufficient to permit of their accurate determination in a sample of not more than 100 cubic centimeters.

These gases usually are: —

1. Carbon dioxide,
2. Benzene,
3. Other heavy hydrocarbons, chiefly éthylene,
4. Oxygen,
5. Carbon monoxide,
6. Hydrogen,
7. Methane (and sometimes ethane),
8. Nitrogen.

Inasmuch as methods for the determination of these various gases have already been described in Chapter XIII, there will

here be given only a description of the successive steps employed in a complete volumetric analysis of coal gas, together with such details of the manipulation as have not previously been discussed.

The Determination of the Absorbable Gases. Apparatus. — In the opinion of the author, the best form of apparatus for the rapid and *accurate* determination of the absorbable constituents of coal gas, numbers 1 to 5 inclusive in the above list, is that of Hempel. The Orsat-Dennis apparatus gives equally good results, but if constructed with the six absorption pipettes that are needed for the removal of the five absorbable gases, it becomes so unwieldy that it cannot be recommended for this purpose.

For usual technical practice, a Hempel gas burette without water jacket may be employed, although somewhat more accurate results can be obtained with the use of a water mantle around the burette. If the room in which the analysis is carried on undergoes fluctuations of temperature, a water-jacketed burette should be used in all cases. The accuracy of the analysis is of course increased by the use of mercury as the confining liquid in the burette, but the differences between the results obtained over mercury and over water are usually not great enough to warrant the employment of mercury in technical practice.

Manipulation. — Clean the burette and level-tube (Fig. 33) and see that the rubber tube on the upper end of the burette is in good condition and is securely fastened in place by the wire ligature. Place an amount of water sufficient for the filling of the burette and level-tube in a flask, and saturate it with the coal gas that is to be analyzed (see p. 59). Fill the burette and level-tube with this water in the manner described on p. 59.

Connect a glass tube to the gasometer or pipe containing the coal gas by means of a short piece of rubber tubing. Pass the gas through this tube until all air has been expelled, insert the

end of it into the rubber tube at the top of the burette, and draw into the burette somewhat more than 100 cc. of the gas. Close the pinchcock at the top of the burette, disconnect the glass tube, and after the water in the burette has run down for one minute measure off a sample of exactly 100 cc. at atmospheric pressure in the manner described on p. 59. Verify the accuracy of this measurement by bringing the water levels in the burette and level-tube to the same height and noting whether the meniscus in the burette stands exactly at the 100 cc. mark.

Carbon Dioxide. — Place a wooden pipette stand at the side of the burette, and, upon the stand, a Hempel gas pipette for the absorption of carbon dioxide (p. 225). Connect the pipette with the burette by either of the procedures described on pp. 61 and 64. Where a number of analyses are to be made one after another, the second method of connecting the pipettes with the burette, described on p. 64, in which a pinchcock is placed upon the rubber tube of the pipette, and the solution in the pipette is driven over to the far bend of the connecting capillary tube and is held there by closing the pinchcock on the pipette, will be found to add much to the convenience of the manipulation and to the rapidity of the analysis. Employ this manipulation in connecting other pipettes with the burette unless there is a reason for not driving the reagent up into the connecting capillary tube, which is the case with fuming sulphuric acid.

Open the pinchcock at the top of the burette, and pass the gas sample into the pipette, allowing the water from the burette to follow to the first bend of the capillary tube of the pipette. After the gas has stood for thirty seconds in the pipette, draw it back into the burette by lowering the level-tube, and bring the solution of potassium hydroxide to the same point in the connecting capillary at which it stood when the pipette and burette were first connected. Disconnect the pipette, allow the water in the burette to run down for one minute, bring the surface of the water in the level-tube to the same height as that in

the burette and read the volume of the residual gas. The diminution in volume measured in cubic centimeters gives directly the percentage of carbon dioxide in the coal gas.

Benzene. — Replace the potassium hydroxide pipette by a double pipette for solid reagents (p. 58) that is charged with a solution of ammonia nickel cyanide (p. 256). Connect the burette with this pipette in the manner employed above and pass the gas repeatedly back and forth between the burette and pipette for a period of three minutes. Pass the gas into the burette, close the pinchcock at the top of the burette, and replace the pipette containing ammonia nickel cyanide by a double pipette for solid reagents that is charged with a five per cent solution of sulphuric acid (p. 257). Pass the gas back and forth about two minutes to remove ammonia.¹ Then draw the gas into the burette, close the pinchcock, allow the water in the burette to run down for one minute as usual, and read the volume of the gas. The difference between this volume and that remaining after the absorption of the carbon dioxide, measured in cubic centimeters, gives the percentage of benzene in the gas.

Other Heavy Hydrocarbons. — Connect the burette by means of a dry capillary tube with a pipette containing fuming sulphuric acid, making the connection and effecting the absorption in the manner described on p. 247.

Draw the gas back into the burette to such point that the acid stands at the original height in the capillary tube of the pipette. Close the pinchcock at the top of the burette, replace the sulphuric acid pipette by one containing potassium hydroxide, and pass the gas into this pipette to remove sulphur trioxide and sulphur dioxide. Drive the acid back into the burette, and measure the decrease in volume after the water has run down for the

¹ If mercury is used in the burette the small amount of water that usually covers its surface will absorb a considerable quantity of ammonia from the reagent. In such case a volume of dilute sulphuric acid amply sufficient to neutralize the ammonium hydroxide thus formed should be drawn over from the pipette into the burette, and then driven back into the pipette.

usual one minute. The difference between this and the last reading gives the percentage of heavy hydrocarbons other than benzene.

Oxygen. — Connect the burette with the pipette containing phosphorus or alkaline pyrogallol or sodium hyposulphite, and remove the oxygen in the manner described in Chapter XIII for the reagent that is employed. The diminution in volume resulting from this absorption gives the percentage of oxygen in the gas.

Carbon Monoxide. — Join the burette to a Hempel double pipette containing ammoniacal or acid cuprous chloride (see p. 232), drive the gas over into the pipette, and hasten the absorption of the carbon monoxide by gently rocking the pipette backwards and forwards for three minutes without disconnecting it from the burette (see p. 63). Draw the gas back into the burette, close the pinchcock of the burette, and replace the pipette with another pipette containing a solution of cuprous chloride that has been but slightly used. Repeat the manipulation and after two minutes shaking pass the gas back into the burette. Some ammonia or hydrogen chloride from the reagent will now be present in the gas mixture. When water is used as the confining liquid in the burette, these gases will be absorbed by it. But when mercury is employed as the confining liquid they should be removed before the gas is measured, the ammonia by passing the gas into a pipette containing 5% sulphuric acid, the hydrogen chloride by passing the gas into a pipette containing potassium hydroxide. Measure the residual volume. The diminution in volume gives the per cent of carbon monoxide in the gas.

Disconnect the cuprous chloride pipette and replace it by a simple pipette (Fig. 34) containing water, and pass the gas residue from the burette into this pipette, allowing the water from the burette to follow over to the lower bend in the long capillary tube of the pipette. Pour out the water in the burette and level-tube, rinse out the tubes first with dilute hydrochloric

acid and then with distilled water, and fill them with distilled water. Pass the gas back again into the burette and measure its volume.

If hydrogen, methane, and nitrogen are to be simultaneously determined in the combustion pipette (see below), the gas residue may be passed directly into this pipette after the determination of carbon monoxide. The burette that is used in the combustion is filled with mercury, not with water.

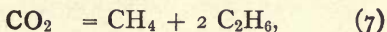
Hydrogen, Methane (and Ethane), and Nitrogen.—

These gases may be determined separately by the successive removal of hydrogen and the paraffins, or if methane is the only hydrocarbon present they may be determined simultaneously by a single explosion or combustion. If ethane is present with methane, the amounts of the two hydrocarbons cannot be determined by combustion unless the hydrogen is first removed (see Chapter XI).

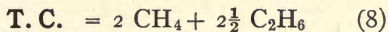
For the *simultaneous* determination of hydrogen, methane and nitrogen, and of methane, ethane and nitrogen the combustion method of Dennis and Hopkins is to be preferred to the explosion of the residue with air or oxygen because in the former procedure the possibility of incomplete combustion or of the formation of measurable amounts of oxides of nitrogen is avoided, and because further the complete oxidation of the combustible gases is independent of the composition of the gas mixture. The manipulation of the combustion pipette for the simultaneous determination of hydrogen, methane and nitrogen, and the calculation of the analytical results is described in detail on pp. 149 and 244. If both methane and ethane are present with hydrogen and nitrogen in the residue remaining after the removal of the absorbable gases, the hydrogen is first removed, and the methane and ethane are then burned in the combustion pipette, the total contraction being noted, and the volume of carbon dioxide formed being ascertained.

The percentages of methane and ethane are then calculated by means of equations 7 and 8 on p. 130.

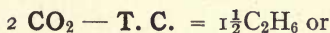
If x represents methane and y ethane, then



and

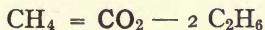


Subtracting the second equation from twice the first



$$\text{C}_2\text{H}_6 = \frac{4 \text{CO}_2 - 2 \text{T. C.}}{3}$$

Then, knowing the volume of ethane,



The *successive* determination of hydrogen, methane (and ethane) and nitrogen may be accomplished in a variety of ways; the hydrogen is first removed, the hydrocarbons are then burned, and the nitrogen is calculated by difference.

Of the many methods for the removal and determination of hydrogen, the most convenient and accurate are the absorption with palladium black (see p. 188), and the fractional combustion with copper oxide (see p. 201). The fractional combustion with palladium asbestos cannot be recommended for the reasons set forth on p. 193 to 196. The Hempel method of fractional combustion with palladium black (see p. 196) removes hydrogen completely, but it is open to the objection that only a small portion of the combustible residue is used, with consequent multiplication of any error that may be made in the measurements.

If the hydrogen is to be removed by absorption with palladium black, the gas burette containing the gas residue is connected with the U-tube containing the palladium black, the amount of air in this U-tube having previously been ascertained by the method described on p. 190. The hydrogen is then absorbed (see p. 189), and the residual gas is drawn back into the burette and measured. The diminution in volume is equal to

the hydrogen in the gas residue plus the oxygen in the air that was originally inclosed in the U-tube when the apparatus was put together. Subtracting this volume of oxygen from the total contraction gives the hydrogen in the gas.

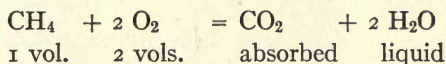
If the hydrogen is to be removed by fractional combustion with copper oxide, the apparatus and method described on pp. 201 to 206 is employed.

After hydrogen has been determined either by absorption with palladium black or by fractional combustion with copper oxide, the tubes used in these methods will still contain some of the combustible residue which must be swept over into the burette with about 30 cc. of nitrogen gas from a phosphorus pipette before the combustion of the hydrocarbons is proceeded with. It is not necessary to know the volume of nitrogen that is hereby added to the gas residue, but the total volume of the residue and the nitrogen that has been added to it must be ascertained by measurement before the combustion is made.

After the removal of the hydrogen, the determination of the hydrocarbons of the paraffin series is next made. If methane is the only hydrocarbon present, the combustion may be carried out in a combustion pipette filled with water because it is here not necessary to determine the volume of carbon dioxide that is formed in the combustion. If, however, the residue contains both methane and ethane, the gas burette and the combustion pipette should be filled with mercury because both the total contraction and the volume of carbon dioxide formed must be ascertained (see p. 315). If methane is the only hydrocarbon present the combustion is carried out as follows:

About 100 cc. of oxygen or of air, if that volume of air contains enough oxygen to insure complete combustion, is run into the combustion pipette, which is then joined to the burette containing the gas residue. The terminals of the pipette are then connected with the source of current, the current is turned on, and the spiral heated to dull redness. The gas residue is slowly passed into the pipette, the current being regulated so that the

spiral will not rise above a dull red heat at any time. When all of the gas has been passed over into the pipette, the platinum spiral is kept at dull redness for 60 seconds. The current is then turned off, the pipette is allowed to cool, and the residual gas is passed back into the burette. Without measuring the residual gas volume at this point, the combustion pipette is detached, and a gas pipette containing potassium hydroxide is connected with the burette. The gas is passed over into this pipette to remove all carbon dioxide and is drawn back into the burette and measured. When methane is burned, one volume of the gas unites with two volumes of oxygen to form one volume of carbon dioxide and two molecules of water. If the carbon dioxide resulting from the combustion is absorbed, the diminution in volume that results from the combustion of one volume of methane equals three times the volume of the gas.



Consequently one-third of the total diminution observed in this combustion equals the volume of methane that is present in the gas residue.

If the residue contains both methane and ethane, the combustion is carried out over mercury, the contraction in volume after the combustion is measured, and the volume of carbon dioxide that has been formed is determined by absorption with potassium hydroxide. The percentage of each of the gases is then calculated by the method given on p. 315.

Nitrogen. — It has hitherto been customary in the analysis of coal gas to state that the amount of nitrogen in the gas is equal to the final residual gas volume after the removal of the absorbable constituents and the combustible gases. Usually, however, small amounts of air are left in the connecting capillary tube when the burette and pipettes are joined together, and these minute air volumes will cause errors that, although negligible in the separate determinations, have a cumulative

effect of considerable magnitude upon the volume of residual nitrogen. For this reason it is preferable to determine nitrogen in a separate sample of the gas.

This may be done by burning a sample of the gas with an excess of oxygen, removing the products of combustion by means of potassium hydroxide, absorbing the excess of oxygen with an alkaline solution of pyrogallol, and measuring the residue, which should be pure nitrogen. The method is carried out as follows:

100 cc. of pure oxygen free from combustible gases, and containing either no nitrogen, or nitrogen of known amount, is placed in the combustion pipette, and a measured amount of the sample of illuminating gas, about 50 cc., is passed from a Hempel burette into the combustion pipette in the usual manner. After combustion is complete the residue is returned to the burette, and carbon dioxide and the excess of oxygen are removed by passing the gas residue successively into a pipette containing potassium hydroxide and one containing alkaline pyrogallol. The residual gas is nitrogen. Since a sample of coal gas less than 100 cc. is used in this determination, the per cent of nitrogen in the gas is not equal to the residual volume, but to

$$\frac{\text{residual volume} \times 100}{\text{volume of sample}}$$

4. *The Determination of Naphthalene in Coal Gas*

Naphthalene is best determined by absorption in picric acid according to the method described on p. 261. Before the gas enters the absorbent, however, it should be freed from tar, cyanogen, hydrogen sulphide and ammonia. This may be accomplished¹ by passing the gas mixture through three wash bottles containing dilute sulphuric acid and then through two wash bottles containing a solution of potassium hydroxide (the authors do not give the strength of these reagents), the five

¹ Albrecht and Müller, *J. f. Gasbeleuchtung*, 54 (1911), 592.

wash bottles being connected glass to glass by short pieces of rubber tubing and being placed in a drying oven heated to about 50°. From the last washing bottle the gas passes through two wash bottles containing picric acid, these bottles being outside of the oven and being connected at their further end with a gas meter and suction pump.

5. The Determination of Total Sulphur in Coal Gas

Illuminating gas that is prepared by the dry distillation of coal always contains compounds of sulphur such as hydrogen sulphide and carbon disulphide. Although the greater part of these products is removed in the purification of the gas before it is admitted to the mains, some of the compounds are always found in the washed gas. These sulphur compounds are objectionable because of the sulphur dioxide that results from their combustion. Inasmuch as all of them form sulphur dioxide when they are burned, the determination of the *total* sulphur in the gas is customarily required, and usually no attempt is made to determine the separate compounds of the element that are present.

The method that is most generally employed for the determination of the total sulphur in illuminating gas consists in burning the gas with the aid of oxygen or air, converting the resulting sulphur dioxide to sulphuric acid, and determining that final product by gravimetric or volumetric means.¹

The two forms of apparatus most generally used for this determination are that proposed by Drehschmidt² and the English "Referees' Test."³ The original apparatus of Dreh-

¹ Among the many articles upon this subject there may be cited the following:

Brügelmann, *Z. f. anal. Chem.*, **15** (1876), 175; Knublauch, *Z. f. anal. Chem.*, **21** (1882), 335; Poleck, *Z. f. anal. Chem.*, **22** (1883), 171; Fairley, *J. Soc. Chem. Ind.*, **5** (1886), 283; Drehschmidt, *Chem. Zeitung*, **11** (1887), 1382; Hempel, *Gasanalytische Methoden*, 3d ed., 1900, p. 255; Witzeck, *J. Gasbeleuchtung*, **46** (1903), 21; Harding, *J. Am. Chem. Soc.*, **28** (1906), 537.

² *Loc. cit.*

³ Abady, *Gas Analysts' Manual*, p. 178.

schmidt is fragile and costly, and because of these characteristics it is inferior to the modification that has been designed by Hempel and that is shown in Fig. 93.

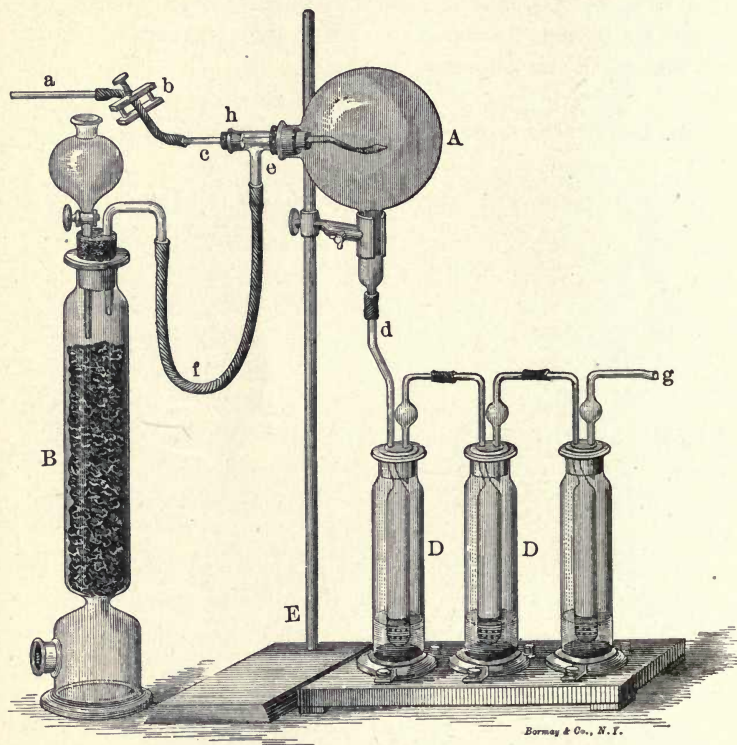


FIG. 93

Determination of Sulphur by Dreh Schmidt-Hempel Method.—The illuminating gas under examination is measured in an experimental gas-meter and then passes through a short piece of rubber tubing *b* and the glass tubing *c* into the flask *A*, Fig. 93. *b* is provided with a screw pinchcock. The tube *c* is of hard glass, is about 5 mm. in diameter, is bent somewhat

downward after it enters the flask and is drawn out at the end to a small opening. The neck of the receiving flask *A* is drawn down in the flame of the blast lamp to a small tube which is connected at *d* by means of a piece of rubber tubing with the absorption apparatus *DD*. The three-way glass tube *e* is inserted in the tubulure of the flask and is held in position in the neck by a piece of rubber tubing or a rubber stopper with a large opening. The side arm of the three-way piece *e* is joined by the rubber tube *f* to the cylinder *B*. This cylinder is filled with pieces of pumice-stone upon which there is allowed to drop a solution of potassium hydroxide from a separatory funnel. The air drawn into the apparatus must pass through this tower and is there freed from any hydrogen sulphide which may be present in the air of the laboratory. *g* is connected with an ordinary water suction pump.

In each absorption bottle *DD* is placed 20 cc. of a 5 per cent solution of potassium carbonate. To the contents of the first two bottles there is added a few drops of bromine to oxidize the sulphur dioxide to sulphuric acid.

The illuminating gas should be allowed to pass through the gas-meter for some time previous to the beginning of the determination, to make sure that the meter is completely filled with the gas under examination.

When the apparatus has thus been prepared for the determination, the water suction pump is started, and a rapid current is drawn through the purifying cylinder *B*, the flask *A*, and the bottles *DD*. The tube *c* is withdrawn from the flask, and the gas is ignited at its outlet. The screw pinchcock *b* is closed until the flame is about 1 cm. long, and *c* is then introduced into *A* and the cork *h* is firmly inserted into position. *c* should be moved in or out through *h* until the flame burns in the middle of the flask. It should lie slightly below the lower side of the tubulure of the flask. In this position the flame will burn quietly for hours, but if it is above the tubulure it will go out, because in the upper part of the flask the products of combustion

are not removed with sufficient rapidity by the entering current of air. By means of the screw pinchcock *b* it is easy so to regulate the flame as to cause it to burn with sharply defined edges, thus insuring complete combustion of the illuminating gas. Note the temperature of the gas, the prevailing barometric pressure, and the reading of the manometer on the meter.

After about fifty liters of the gas has been burned, read the meter accurately and remove the burner from the globe. At this point the barometer, the manometer on the meter, and the thermometer should be read again and the average value should in each case be used in the calculation of results.

Rinse the globe with distilled water into a beaker. Pour the contents of the three (Muencke) wash bottles into the beaker and rinse well with distilled water. Acidify the solution with hydrochloric acid and heat to boiling in order to expel the bromine. Add barium chloride to the hot solution and determine the weight of barium sulphate in the usual manner.

The sulphur, which may exist in the gas as hydrogen sulphide, as carbon disulphide, or as organic sulphur compounds, is burned to sulphur dioxide, SO_2 , which is oxidized by the bromine to sulphur trioxide, SO_3 , and this reacts with the potassium carbonate to form potassium sulphate. Hydrochloric acid is added to the solution to decompose the carbonate present.

The amount of sulphur in the gas is calculated from the weight of the barium sulphate found, the result being expressed in terms of grams of sulphur per cubic meter (1000 liters) of the gas at 0° and 760 mm.

Grams sulphur per cubic meter =

$$\frac{1000}{V} \times (P - P_1) \frac{\text{At. wt. sulphur}}{\text{Mol. wt. BaSO}_4} \times \frac{760 (1 + 0.00367t)}{(B + b) - m}$$

In the above

V = liters of gas burned,

P = grams BaSO_4 found,

P_1 = grams BaSO_4 found in blank test of reagents,¹

B = observed barometric pressure,

b = pressure (in addition to atmospheric) of gas in meter,

t = temperature of gas in meter,

m = tension aqueous vapor at t° .

$$\frac{\text{At. wt. S}}{\text{Mol. wt. BaSO}_4} = 0.137325.$$

To express results as "grains sulphur per 100 cubic feet of the gas," multiply "grams per cubic meter" by the factor 43.698.

Schumacher and Feder² state that only sulphur dioxide and no sulphur trioxide is formed in the combustion of the gas in the Drehschmidt apparatus. Upon this observation they base a volumetric method for the determination of total sulphur.

A measured volume of a solution of potassium iodate of known strength, that contains about 18 grams of potassium iodate to the liter, is placed in the absorption bottles *DD*, and the gaseous products of the combustion are drawn through this liquid in the usual manner. The solution is then transferred to a flask and is boiled for from ten to fifteen minutes to expel the liberated iodine. The liquid is then cooled, a little sulphuric acid is added, and the excess of potassium iodate is titrated with sodium thiosulphate. The authors state that the results agree quite satisfactorily with those obtained by the gravimetric method.

In the use of the Hempel modification of the Drehschmidt apparatus difficulty is at times experienced in so regulating the combustion in the flask *A* that the flame will be non-luminous and at the same time will burn continuously throughout the run. Harding states³ that this difficulty may be avoided by the

¹ The bromine water and potassium carbonate used should be tested qualitatively for the presence of sulphates. If the test gives positive results the sulphur is determined in a quantity of these reagents equal to that used in the experiment.

² *Z. f. Unters. Nahr.-Genussm.*, 10 (1905), 649.

³ *J. Am. Chem. Soc.*, 28 (1906), 537.

use of a special burner of hard glass which is figured and described in his article.

Determination of Sulphur by Referees' Method.— The official method in use in London, England, for the determination of the total sulphur in illuminating gas is known as the Referees' Test.¹

In this method the gas is burned in air that contains ammonia, and the resulting water, ammonium carbonate, ammonium sulphite, and ammonium sulphate are collected in a condensing tower. The products of combustion are then dissolved in water, the solution is acidified with hydrochloric acid and is boiled to expel carbon dioxide. The sulphate that is present is then precipitated with a solution of barium chloride. The accuracy of the method has been called in question because of the possibility of incomplete retention of the oxides of sulphur by the condensing tower, and further because of the probability that some of the sulphur would be oxidized only to sulphur dioxide,² in which case the resulting ammonium sulphite would be decomposed when the solution is boiled with hydrochloric acid and some sulphur would escape precipitation as barium sulphate. These points have been investigated in the Cornell Laboratory by Mr. George Hopp. He found that the condensing tower that is customarily used will retain the oxides of sulphur if the rate of flow of the gas does not exceed twenty liters per hour. As to the second point, however, his analyses show that the Referees' method yields too low results unless the solution of the products of combustion is treated, before acidification, with an oxidizing agent that will convert the sulphite to sulphate. With these modifications the method appears to give quite satisfactory results.

In the Referees' method the gas is burned in a Bunsen burner *B*, Fig. 94, that stands in a perforated metal base *D*. The burner

¹ A detailed description of this procedure is given in Abady's *Gas Analysts' Manual*, Chapter V.

² In this connection see Schumacher and Feder, *Zeit. f. Unters. Nahr.-Genussm.*, 10 (1905), 649.

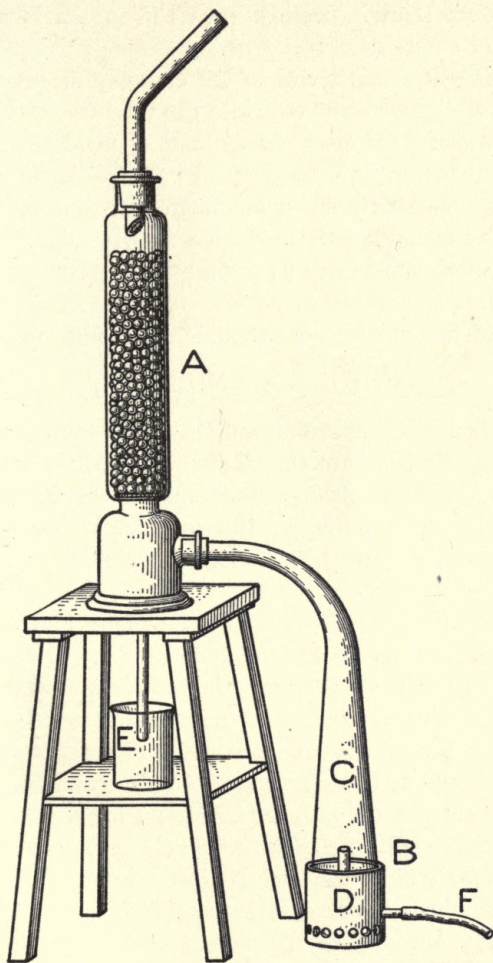
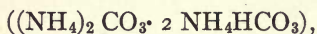


FIG. 94

that is furnished with the apparatus is a small Bunsen burner with a steatite tip. With an ordinary Bunsen burner, however, the gas can be burned more rapidly, without the formation of a

smoky flame, than is possible with the special burner. The products of combustion pass upward through the conical glass chimney *C*. The upper end of the chimney passes through a rubber stopper that is inserted into the tubulure of the cylinder *A*. The upper portion of the cylinder is filled with pieces of glass rod about 40 mm. long and 8 mm. in diameter, or with glass balls about 15 mm. in diameter. In the bottom of the cylinder is a round hole into which is inserted a rubber stopper that carries a glass tube. The condensed water flows through this tube into the beaker *E*.

Pieces of non-effloresced ammonium sesquicarbonate,



about 40 grams in all, are placed around the burner on a perforated plate in the base *D*. A few pieces of the salt are also placed on top of the glass rods or balls in the cylinder. The ammonia that is set free by the spontaneous decomposition of this substance unites with the sulphur dioxide and prevents its escape.

The gas is first passed through a gas meter until all air has been driven from the meter and the water in the meter is saturated with the gas under examination. The meter is then connected with the burner *B* and the gas is lighted at the burner. The flame is turned down until the rate of consumption of gas is not more than 20 liters per hour. A screw clamp placed upon the rubber tube of the burner furnishes a means of accurately adjusting the height of the flame. The burner and the base *D* are then placed under the conical glass chimney and the upper end of the chimney is at once inserted into the opening of the cylinder *A*. Readings of the meter, the barometric pressure, the manometer on the meter and the temperature of the gas as it passes through the meter are immediately made.

When from 50 to 60 liters of gas has been burned, the gas is turned off and the instruments that were read at the beginning of the run are now read again. The averages of the readings

of the barometer, thermometer and manometer are used in the calculation of results. The beaker *E* is replaced by a clean empty beaker and the cylinder *A* is rinsed by pouring through the tube attached to the upper opening of the cylinder two or three portions of distilled water of 25 cc. each. The chimney *C* is also rinsed out with distilled water into the beaker. These rinsings are then added to the contents of the first beaker. A measured amount, about 2 cc., of saturated bromine water is added and the liquid is thoroughly stirred for a few moments.¹ The solution is acidified with hydrochloric acid and is heated to boiling to decompose the carbonates that are present and to expel the excess of bromine. A solution of barium chloride is then added and the precipitate of barium sulphate is collected on a filter and is washed, dried, and weighed in the usual manner. The amount of sulphur in the gas is calculated from the weight of the barium sulphate by means of the formula given on p. 322.

Young's Volumetric Method for Determination of Sulphur. — Young has proposed² an indirect volumetric method for determining the sulphur in illuminating gas. The solution of the sulphates obtained by the Referees' method is treated with bromine water in the manner above described and then acetic acid is added in an amount sufficient to decompose the ammonium carbonate³ that is present. The solution is then made up to definite volume and to a measured portion of it there is added a measured excess of a standard solution of barium chloride. The precipitated barium sulphate is not removed by filtration, but solution and suspended precipitate are transferred to a platinum or porcelain dish and the whole is evaporated to dryness and is then heated to low redness to expel the hydrochloric acid and ammonium chloride. The dish is allowed to cool and the con-

¹ If the bromine water contains sulphates, the amount of sulphur in the volume of this reagent that is added should be subtracted from the final result. Ammonium sesquicarbonate usually contains no sulphate, but it nevertheless should be tested for this impurity before being used.

² Stone's *Practical Testing of Gas and Gas Meters*, p. 116.

³ These chemicals must be free from non-volatile halogen salts.

tents is washed out with distilled water into a beaker. An amount of a 10% solution of potassium chromate sufficient to precipitate all of the barium chloride and to color the supernatant liquid pale yellow is then added, and a standard solution of silver nitrate is run in from a burette until the red color of silver chromate remains permanent. The solutions that are here used are a $\frac{N}{20}$ solution of silver nitrate that contains 8.449 grams AgNO_3 to the liter and a $\frac{N}{4}$ solution of barium chloride that contains 26.0375 grams BaCl_2 to the liter. In the calculation of results the volume of the gas that has been burned is corrected to standard conditions (760 mm., 0°C.). The volume of barium chloride equivalent to the volume of silver nitrate that has been added (5 cc. $\text{AgNO}_3 = 1 \text{ cc. BaCl}_2$) is then calculated, and this result is subtracted from the volume of barium chloride that was added. The remainder represents the amount of barium chloride that reacted with the sulphate in the solution. Knowing the strength of the solution of barium chloride, the actual weight of the barium chloride may then easily be calculated, and from this the grams of sulphur in the corrected volume of gas that has been burned. This final result should then be converted into the amount of sulphur in grams per cubic meter of the gas, or in grains per one hundred cubic feet of gas.

6. The Determination of Cyanogen in Coal Gas

For the determination of the total cyanogen in illuminating gas the method of Nauss (p. 263) may be used.

PINTSCH GAS

Pintsch gas is made by the destructive distillation of crude petroleum or its distillates. It possesses an illuminating power three or four times greater than that of average coal gas, and it can be brought under a pressure of ten atmospheres with a loss of only ten per cent of its illuminating power. Twenty-five

samples of the compressed gas showed on analysis the following average composition:

Heavy Hydrocarbons (Illuminants)			
Benzene, C_6H_6	}	. . .	35 per cent
Ethylene, C_2H_4 , etc.			
Propylene, C_3H_6			
Carbon Monoxide, CO		0.5	"
Hydrogen, H_2		4.5	"
Methane, CH_4	}		60 "
Ethane, C_2H_6			

In the analysis of a sample of Pintsch gas the constituents would be determined in the order already given under illuminating gas, namely: —

Carbon dioxide by absorption with potassium hydroxide,

Benzene by absorption with ammonia nickel cyanide and 5 per cent sulphuric acid,

Heavy hydrocarbons other than benzene by absorption with fuming sulphuric acid and potassium hydroxide,

Oxygen by absorption with alkaline pyrogallol,

Carbon monoxide by absorption with ammoniacal cuprous chloride,

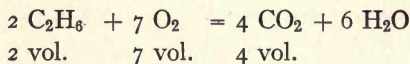
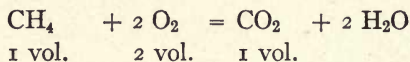
Hydrogen by fractional combustion with copper oxide (p. 201) or by absorption with palladium-black (p. 188),

Methane and ethane by combustion with oxygen in the combustion pipette (p. 149), and calculation of the percentages of the two gases by the method set forth on p. 315.

The high percentage of heavy hydrocarbons in Pintsch gas renders it necessary that the treatment of the mixture with the absorbents for these constituents be thorough and sufficiently prolonged to insure the complete removal of these gases.

The large amount of methane and its homologues precludes the use of the total residue in the final combustion if, as is desirable, the volume of oxygen and the volume of the resulting carbon dioxide are to be kept within the capacity of the gas

burette (100 cc.). This is apparent from the equations representing the combustion of methane and ethane.



Consequently, in the combustion of methane and ethane in Pintsch gas, 100 cc. of oxygen is first passed into the combustion pipette and then only such portion of the combustible residue is introduced as will ensure the presence of an excess of oxygen in the pipette after the combustion is complete.

It is not possible, by means of one complete combustion, to determine more than two hydrocarbons of the methane series (see p. 130, First Case). For this reason, if the combustible residue contains, in addition to methane and ethane, a higher homologue of the series, this third hydrocarbon cannot be determined by the above procedure. It is usually satisfactory, however, to consider that the combustible residue, after the removal of hydrogen, contains only methane and ethane and to calculate the results on the basis of that assumption.

PRODUCER GAS — BLAST-FURNACE GAS

In the analysis of these gas mixtures the determination of benzene may be omitted but no further special modification of the usual procedure is needed unless the combustible residue is to be determined by explosion. Producer gas and blast-furnace gas frequently contain so small an amount of combustible gas that the residue will not explode when mixed with oxygen or air. In such case pure hydrogen or oxyhydrogen gas must be added to the residue (see p. 144).

CHAPTER XVI

THE DETERMINATION OF THE HEATING VALUE OF FUEL

The heating value of a fuel is determined by burning a known amount of the fuel in an apparatus termed a fuel calorimeter and measuring the heat that is produced.¹

Fuel calorimeters are of two types, *continuous* and *discontinuous*. The heating value of solid fuels is usually determined with a calorimeter of the discontinuous form, while with liquid and gaseous fuel a continuous calorimeter is customarily employed.

1. *The Determination of the Heating Value of Solid Fuels*

The most satisfactory and accurate method for the determination of the heating value of solid fuel consists in burning a weighed amount of the fuel with the aid of compressed oxygen in a bomb that is immersed in water. The heat evolved in the combustion warms the water that surrounds the bomb and from this rise in the temperature of the water the heating value of the fuel is calculated.

The Bomb. — Of the many forms of bombs that have been devised, the best known types are those of Berthelot, Mahler, Hempel, Atwater, Kröcker, Emerson and Langbein. That designed by Mahler will here be described.

The Mahler bomb (Fig. 95) is a steel cylinder *B* of 10 cm. external diameter at the lower end and 14 cm. high, with walls

¹ For full discussion of this subject, see *Kalorimetrische Methodik*, by W. Glikin, 1911; *Die kalorimetrische Heizwertbestimmung von Kohle mit besonderer Berücksichtigung der Kalorimeteereichung*, Jacob, *Zeitschrift für chemische Apparatenkunde*, 2 (1907), 281, 313, 337, 369, 499, 533, 565, 597; *Circular of the Bureau of Standards*, No. 11, *The Standardization of Bomb Calorimeters*.

8 mm. thick. The outer surface is nickel-plated; the inner surface is usually covered with white enamel, although some of the finer instruments are lined with platinum or gold. The

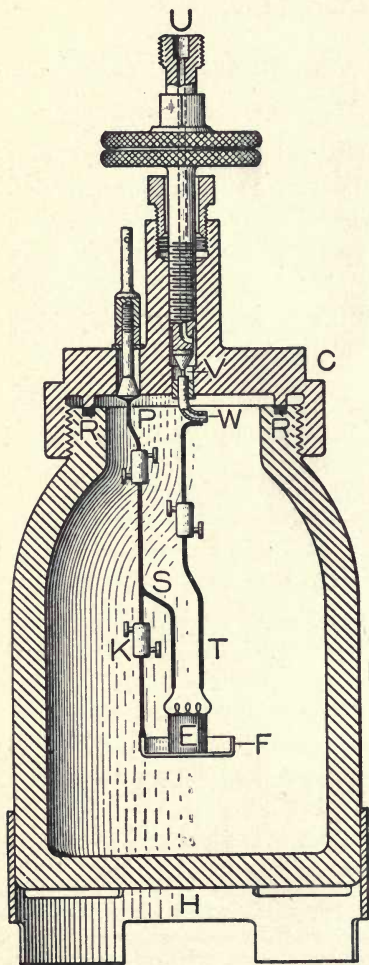


FIG. 95

bomb rests in a nickel-plated sheet iron saddle *H* which renders possible the free circulation of water between the bottom of the calorimeter vessel and the bottom of the bomb. The bomb is closed by a steel cover *C* which also is nickel-plated on the outside and enamelled on the inside. The joint between the bomb and the cover *C* is made gas tight by setting into the top of the bomb a lead gasket against which a projecting ring *R* on the under side of the cover impinges when the cover is screwed down into place. Compressed oxygen is passed into the bomb through the opening in the stem of the needle valve *V* and the tube *W*. The bomb is closed by screwing down the valve *V* until the conical lower end is pressed against the opening that leads into the bomb. A platinum rod *P* passes through the cover of the bomb and is insulated from

the metal of the cover. Another platinum rod *S*, about one mm. in diameter and of the form shown in the figure, is fastened to the lower end of *P* by means of a small binding post. A platinum rod that carries a platinum plate *F* is fastened by a binding post *K* to the lower end of *S*. The plate *F* is about 28 mm. in diameter, and has sides about 4 mm. high. Soldered to the lower end of the tube through which the oxygen is admitted is another platinum rod which is joined by a binding post to the platinum rod *T*. *T* extends downward to the same distance as the branch rod from *S*.

The fuel is placed in the platinum pan *F* and is ignited by passing an electric current through a fine iron wire of about 0.15 mm. diameter that is wrapped around the lower ends of the wires *S* and *T* and rests against the fuel.

Preparation of Sample of Coal. — The substance, usually coal, whose heating value is to be determined, should be accurately sampled and pulverized to pass a 100-mesh sieve. Coal should be air-dried, the loss in weight on drying being determined and the heating value calculated back to the undried coal.

The sample of the air-dried coal that is to be used for the combustion may be handled with greater convenience and with less danger of loss if the coal is first compressed into a compact mass or briquet by means of such a press as that shown in Fig. 96. The cylindrical opening *A* in the steel block *H* is filled with the powdered sample which is then compressed to a coherent mass by turning the bar *B* and driving down the plunger *C*. The small cylinder of coal is then pushed out of *A* by turning the screw *S* upward, inserting the steel plate *P* that carries *H* into the slot *KK* and again driving down the plunger *C* upon the coal cylinder in *A*.

This compression of the coal to the form of a briquet does not appear to be necessary, so far as accuracy of result is concerned, in the case of anthracite coals. These coals may be weighed

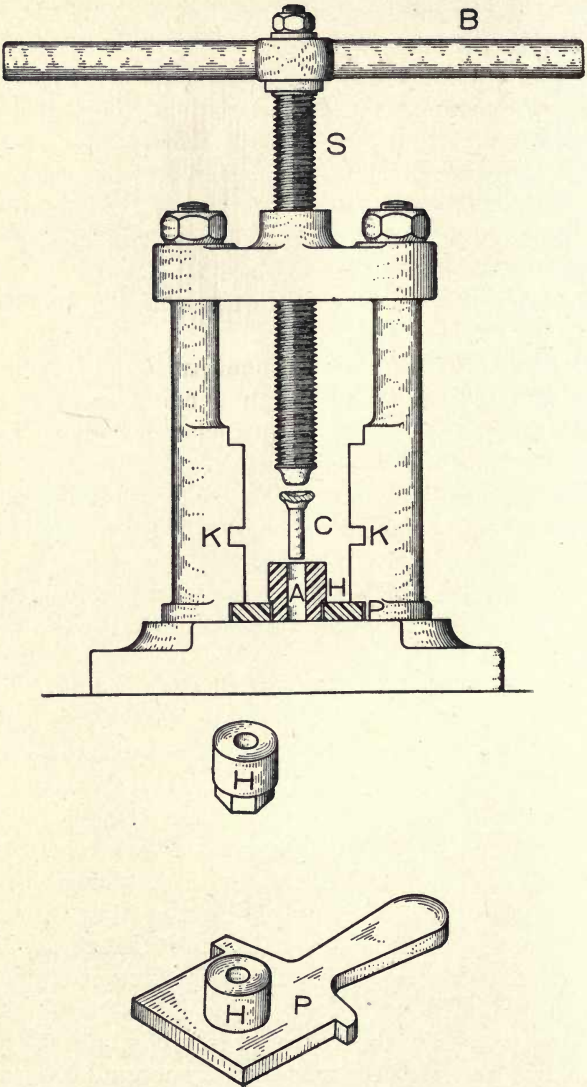


FIG. 96

in powdered form directly into the platinum pan *F*. With bituminous coal, however, it frequently happens that an appreciable amount of the powdered sample is thrown out of the platinum pan by the violent escape of volatile matter during the combustion in the bomb, and, after the combustion, the interior of the bomb will frequently be found to be covered with a fine, black dust. The degree to which a powdered bituminous coal may escape combustion in the bomb is shown by the results of an examination into this subject made for the author by Mr. N. R. Beagle. Mr. Beagle found that it was practically immaterial whether an anthracite coal be compressed into a briquet or burned in the powdered form. But with a bituminous coal he obtained an average result of 7170 calories per gram when the fuel was burned in the powdered form and 7308 calories per gram when the bituminous coal was briqueted. The interior of the bomb after combustion showed unburned coal dust in each case when powdered coal was used, whereas when the coal briquet was employed, none of this powder was visible after combustion.

If the coal is compressed, the little cylinder of coal is freed from coal dust by brushing it with a camels' hair brush and is then trimmed with a knife to the proper weight. The coal sample should weigh about one gram. The sample, *E*, is then placed in the platinum pan *F* and is accurately weighed.

The Calorimeter. — The calorimeter vessel is a nickel-plated metal cylinder *J* (Fig. 97) that should be just large enough to permit of complete immersion of the bomb and thorough stirring of the water. It is supported in a double-walled metallic vessel *K* that is enamelled on the surface next to the calorimeter, and is provided with a metallic cover that has openings, *w w*, through which this jacket may be filled with water. This vessel is further covered on the sides and top and bottom with a layer of felt about one centimeter thick. The calorimeter vessel is placed within the jacket vessel *K* in the position shown in the figure and this inner opening of *K* is provided with a cover *R* that is made

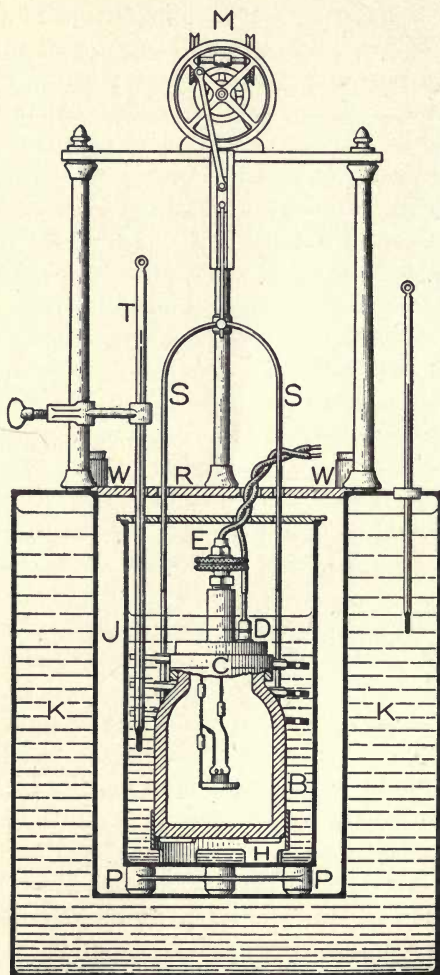


FIG. 97

in two pieces and that has openings through which pass the thermometer *T* and the rods of the stirrer *SS*. The thermometers that are used in this work are usually filled with mercury and

have the scale marked on the stem. They should cover a range of 10° to 15° C. with graduations in 0.01° , or should be of the Beckmann type with a scale range of about six degrees. Before being placed in use the thermometers should be tested and the corrections for errors in the scale ascertained. The stirrer may be run by a motor or may be operated by hand. The stirring should be slow and in all cases as uniform as possible.

The calorimeter vessel should not rest directly upon the metal jacket but should stand upon supports *PP* of glass, porcelain or ebonite. The stirrer should be of the screw type, but should move straight up and down. The rotary movement of the stirrer in the usual form of Mahler calorimeter makes it impossible to adequately cover the inner calorimeter vessel.

Preparation of the Bomb. — Clean the inside of the bomb and polish the nickel surface of the bomb and its cover. Place the cover of the bomb in an upright position in a clamp or on a ring stand. Wind a piece of iron ignition wire (see above) about 3 cm. long around a pin to give it spiral form and then weigh the wire. If the apparatus is in frequent use, it will be found more convenient to ascertain the weight of the ignition wire per linear centimeter and then to measure the length of the piece that is used.

Wrap the ends of the ignition wire around the platinum wires *S* and *T* (see Fig. 95). Clean the platinum plate *F*, place within it the weighed coal briquet *E* or the powdered coal, and then fasten it to *S* by means of the small binding post *K* in such position that the spiral of ignition wire rests lightly against the top of the coal.

Introduce from 0.5 to one cc. of water into the bomb, place upon the bomb the cover carrying the coal sample, screw down the cover with the hand, and finally set it down firmly with a wrench.

To fill the bomb with compressed oxygen, proceed as follows:

Connect to *U*, Fig. 95, by means of a nut the flexible copper tube *L* (Fig. 98) that leads to the manometer *M* and the oxygen

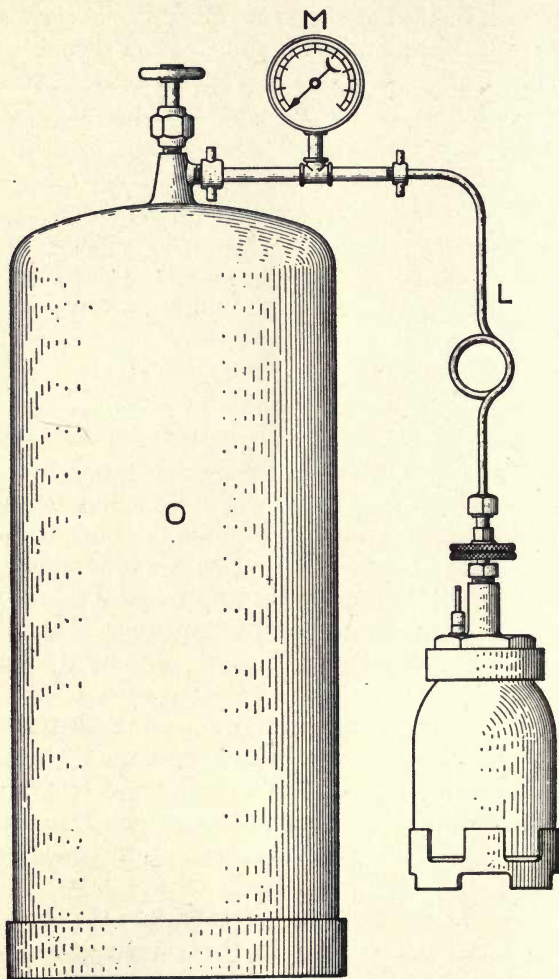


FIG. 98

tank O.¹ Open the valve of the oxygen tank slowly and allow the

¹ The oxygen should of course contain no combustible gases such as carbon monoxide, hydrogen or hydrocarbons.

pressure in the bomb to rise to about five atmospheres. Close the valve of the bomb, disconnect the copper tube *L*, and then carefully open the valve *V*, Fig. 95. This operation serves to rinse out the bomb with oxygen and thus to remove the greater part of the nitrogen of the air that was originally in the bomb. This is done to prevent the formation of an appreciable amount of nitric acid from atmospheric nitrogen during the combustion. The correction for the heat of formation of nitric acid is, however, usually less than six calories, a value so small that the rinsing of the bomb with oxygen may be omitted in most commercial work.

Now connect *L* again with *U*, open the valve of the oxygen tank carefully and fill the bomb with oxygen to a pressure of 25 atmospheres. Close the valve *V* and disconnect *L*.

Combustion of the Sample. — Fill the jacket space of the calorimeter with water of a temperature about that of the room. Place the bomb, prepared for the combustion as above described, in the calorimeter and connect its terminals by wires with the apparatus that is to furnish the electric current for the heating of the iron ignition wire. Storage cells or dry cells that will yield a current of a potential of not more than 15 volts should be employed. If a 110-volt lighting circuit is used there is danger of arcing and consequent evolution of heat within the bomb. The battery and ignition wire should previously be tested to make sure that the current will heat the wire to incandescence in the space of one second. Pour into the calorimeter vessel that contains the bomb a weighed amount of water of a temperature of from $1\frac{1}{2}^{\circ}$ to 2° below that of the room. The same amount of water should be used in all combustions. The volume necessary for the complete immersion of the bomb will vary in different calorimeters from about 2200 cc. to 2700 cc.

Introduce the stirrer and the thermometer and then put on the cover of the calorimeter. Begin stirring and continue it for about five minutes. At the end of this time the temper-

ature should be constant or should be regularly and only slightly rising or falling. Now begin readings of the thermometer in the calorimeter, noting the time in hours, minutes and seconds, and repeat these readings every minute for a period of five minutes in all. These five readings cover what is termed the "preliminary period." Throughout the whole experiment the water in the calorimeter should be stirred at a uniform rate between all readings.

At the end of the preliminary period, throw in the switch (preferably exactly on an even minute) and ignite the substance. Throw out the switch at the end of one second. Read the thermometer every twenty seconds, recording the time of each reading as before. Continue these readings every twenty seconds until the maximum temperature has been reached and the temperature begins to fall. This ends the "middle period."

From this point make readings one minute apart over a period of time equal to the length of the preliminary period. This constitutes the "after period." Remove the bomb from the calorimeter and slowly open the valve to relieve the excess of gas pressure within the bomb. Then unscrew the cover of the bomb and examine the interior of the bomb to make sure that the fuel was completely burned.

The Water Equivalent of the Calorimeter. — When a sample of fuel is burned in the bomb, the greater part of the heat that is evolved is transferred to the surrounding water which is thereby raised in temperature. The remainder of the heat is taken up by the apparatus itself. Each particular apparatus will have a definite heat capacity of its own, which will be different from that of another apparatus even of the same type. It is customary to express the heat capacity of the instrument in terms of the number of grams of water that would be raised 1°C. in temperature by the heat absorbed by the apparatus. This result is termed the *Water Equivalent* of the calorimeter. It should experimentally be ascertained with great care for each

instrument, because an error in this will affect all determinations made with the calorimeter.

The water equivalent of most of the bomb calorimeters now on the market is determined by the manufacturer and is marked upon the instrument. If, however, the calorimeter is not so marked, or if the operator deems it desirable to ascertain the correctness of the marking, the water equivalent of the apparatus may be determined *once and for all* —

(a) By weighing the different parts of the apparatus, multiplying the weight of each part by the specific heat of the material of which that part is made, and adding the results: or

(b) By the method of mixtures:¹ or

(c) By setting free a known amount of heat within the bomb and ascertaining the resulting rise of temperature of the water in the calorimeter vessel. The most accurate results by this method are obtained by the insertion of an electric resistance heater within the bomb, but usually the determination is made by burning in the bomb a weighed sample of a combustible substance whose heat of combustion has accurately been ascertained.

Standard Combustible Substances. — The combustible substances in most general use as standards are cane sugar, benzoic acid and naphthalene. Samples of these substances, specially prepared for this purpose, may be obtained from the Bureau of Standards at Washington. Circular No. 11 of the Bureau contains the following statement concerning these three materials:

“Sucrose is not volatile nor strongly hygroscopic, but is rather difficult to ignite and sometimes does not burn completely. It has a heat of combustion of about 3950 calories, or only about half that of the average coal. The more exact value for each sample will be given in the certificate.

“Benzoic acid is only slightly volatile, is not very hygroscopic,

¹ See Jakob, *Z. f. chem. Apparatenkunde*, 11 (1907), 533.

has a heat of combustion of about 6320 calories and burns more readily than sugar.

"Naphthalene is quite volatile but not hygroscopic; it has a heat of combustion of about 9610 calories, a little higher than that of most coals, and it ignites and burns very readily.

"Of these materials probably the most satisfactory for work of the highest accuracy is benzoic acid, but for calibration of commercial calorimeters to an accuracy of 0.1 per cent naphthalene has some advantages. The loss by sublimation from samples of naphthalene made up into briquets will hardly exceed 0.1 or 0.2 per cent in an hour."

This last mentioned method is the most satisfactory for the calibration of commercial calorimeters. It is carried out as follows: Compress some of the standard combustible substance in the press into the form of a briquet, trim it down until it weighs about one gram,¹ free it from loose particles and dust, and burn it in the calorimeter in the manner already described.

EXAMPLE OF THE DETERMINATION OF THE WATER EQUIVALENT OF A CALORIMETER

Readings on Beckmann Thermometer During the Experiment

PRELIMINARY PERIOD		MIDDLE PERIOD		AFTER PERIOD	
Time	Temp.	Time	Temp.	Time	Temp.
2:30:00	2.430°	2:35:20	2.54°	2:41:30	4.750°
31:00	2.434	36:00	3.26	42:00	4.747
32:00	2.438	36:20	4.16	43:00	4.743
33:00	2.443	36:40	4.46	44:00	4.737
34:00	2.446	37:00	4.62	45:00	4.732
35:00	2.450	37:20	4.70	46:00	4.728
Sample ignited		37:40	4.73		
		38:00	4.75		
		38:20	4.751		
		38:40	4.752		
		39:00	4.753		
		39:20	4.753		
		39:40	4.753		
		40:00	4.753		
		40:20	4.753		
		40:40	4.753		
		41:00	4.753		

¹ The amount of the substance should be such as will cause about the same rise in temperature in the calorimeter as that which results from the combustion of about one gram of the fuels that are later to be tested.

Weight of sample of benzoic acid	1.0020 grams
Weight of water in calorimeter	2250 grams
Weight of iron ignition wire	0.004 gram
Pressure of oxygen in the bomb	25 atmospheres

Reading of thermometer at end of middle period	4.753°
Reading of thermometer at beginning of middle period	2.450°
Observed rise of temperature	2.303°
Radiation correction (see below)	+ .019°
Corrected rise of temperature	2.322°

Heat of combustion of benzoic acid in calories per gram	6320
Heat evolved by combustion of sample of benzoic acid taken	$1.0020 \times 6320 = 6332.6 \text{ cal.}$
Heat of combustion of iron in calories per gram	1600
Heat evolved by combustion of ignition wire	$0.004 \times 1600 = 6.4 \text{ cal.}$
Heat evolved by combustion of sample	$\frac{6339}{6339} \text{ cal.}$

Total weight of water that would be raised 1° C. in temperature by heat evolved	$\frac{6339}{2.322} = 2730 \text{ grams.}$
---	--

Water equivalent of calorimeter, or total weight of water that would be raised one degree in temperature, less the weight of the water in the calorimeter vessel	$2730 - 2250 = 480 \text{ grams.}$
--	------------------------------------

The Radiation Correction. — If the calorimeter could be perfectly insulated from its surroundings, the only temperature observations that would be necessary for the determination of the water equivalent of the apparatus or of the heating value of a fuel would be the temperature of the water before the ignition and after the combustion. Perfect insulation is, however, impossible, and there is a continuous transfer of heat between the calorimeter and its surroundings, due to conduction, radiation,

convection currents of air and evaporation of water in the calorimeter. This heat transfer will affect the thermometric readings and consequently a correction, termed the *radiation correction*, must be applied to eliminate the errors due to gain or loss of heat by the calorimeter during the determination. Among the various methods for ascertaining the radiation correction that are in use,¹ the following will be found satisfactory and sufficiently accurate for commercial work. In this, the average rate of heat transfer between the calorimeter and its surroundings during a period of, say, five minutes, before the ignition of the fuel, "Initial Radiation Rate," and for a like period after the maximum temperature resulting from the combustion has been reached, "Final Radiation Rate," is computed. The time at which the mean temperature of the combustion period is reached is then calculated, and the initial radiation correction is computed for the first part of the middle period, and the final radiation correction for the last part. From these results the corrected rise in temperature during the combustion is obtained. The radiation correction is determined for each run of the calorimeter. In the example of the determination of the water equivalent of the apparatus given above the radiation correction is calculated in the following manner:

$$\begin{aligned} \text{Radiation Rate, Preliminary Period,} &= \\ \frac{2.45^{\circ} - 2.43^{\circ}}{5} &= 0.004^{\circ} \text{ per minute }^2 \end{aligned}$$

$$\begin{aligned} \text{Radiation Rate, After Period,} &= \\ \frac{4.753^{\circ} - 4.728^{\circ}}{5} &= 0.005^{\circ} \text{ per minute }^3 \end{aligned}$$

¹ See *Experimental Engineering* by Carpenter and Diederichs, 7th ed., 1911, p. 482.

² This correction is positive if the temperature is falling during the preliminary period and negative if it is rising.

³ This correction is positive if the temperature is falling during the after period and negative if it is rising.

Mean Temperature of Middle Period =

$$\frac{2.45^{\circ} + 4.753^{\circ}}{2} = 3.601^{\circ}$$

Time at which mean temperature was reached (ascertained by plotting curve, or by interpolation), 2:36:10.

Portion of middle period to which correction for "preliminary" radiation rate is to be applied, 2:36:10 — 2:35 =

$$1 \text{ min., } 10 \text{ sec.} = 1\frac{1}{6} \text{ min.}$$

Portion of middle period to which correction for "after" radiation rate is to be applied, 2:41:00 — 2:36:10 =

$$4 \text{ min., } 50 \text{ sec.} = 4\frac{5}{8} \text{ min.}$$

Radiation Correction =

$$0.005^{\circ} \times 4\frac{5}{8} - 0.004^{\circ} \times 1\frac{1}{6} = 0.019^{\circ}$$

Example of the Determination of the Heating Value of a Sample of Coal. —

Weight of sample of coal 1.0050 grams

Weight of water in the calorimeter 2250 grams

Weight of iron ignition wire 0.004 gram

Pressure of oxygen in bomb 25 atm.

PRELIMINARY PERIOD		MIDDLE PERIOD		AFTER PERIOD	
Time	Temp.	Time	Temp.	Time	Temp.
11:02:00	2.910°	11:07:20	2.96°	11:14:00	5.498°
03	2.916	07:40	3.03	15:00	5.493
04	2.922	08:00	3.18	16:00	5.490
05	2.928	08:20	3.70	17:00	5.486
06	2.934	08:40	4.22	18:00	5.482
07	2.940	09:00	4.70		
Coal ignited		09:20	5.06		
		09:40	5.26		
		10:00	5.40		
		10:20	5.46		
		10:40	5.49		
		11:00	5.500		
		11:20	5.501		
		11:40	5.502		
		12:00	5.502		
		12:20	5.502		
		12:40	5.502		
		13:00	5.502		

From these data the heating power of the coal is calculated by use of the formula:

$$H = \frac{(W + E) (T \pm R) - C}{G}$$

in which H represents the heating value of the fuel, W the weight of the water in the calorimeter vessel, E the water equivalent of the calorimeter, T the rise in temperature caused by the combustion, R the radiation correction, C the heat of combustion of the iron ignition wire, and G the weight in grams of the sample of fuel.

In the above example

$$W = 2250 \text{ grams}$$

$$E = 480 \text{ grams}$$

$$T = 2.562^{\circ} \text{ C.}$$

$$R = + 0.007^{\circ} \text{ C.}$$

$$C = 6.4 \text{ calories}^1$$

$$G = 1.0050 \text{ grams}$$

$$H = \frac{(W + E) (T + R) - C}{G} =$$

$$\frac{(2250 + 480) (2.562 + 0.007) - 6.4}{1.005} = 6972 \text{ calories per gram.}$$

It is customary in this country to express the heating value of a fuel in terms of British thermal units² (B. T. U.) per pound of

¹ Correction is sometimes introduced for the heat of formation of nitric acid that is formed by the oxidation of nitrogen gas in the bomb. This is done by washing out the bomb with distilled water after the combustion and titrating the acid with a standard solution of an alkali. The correction is so small that it may be disregarded in commercial work. If the bomb is rinsed with oxygen gas before the combustion, the amount of nitric acid that is formed from the atmospheric nitrogen in the bomb will be so slight as to be negligible even in quite accurate work. Moreover sulphurous acid and sulphuric acid that result from the combustion of the sulphur in the coal are frequently found in the bomb after the combustion. The presence of these compounds will vitiate the titration results for nitric acid. Furthermore their heat of formation should not be subtracted from the heating value of the fuel.

² A British thermal unit is the amount of heat required to raise the temperature of one pound of water one degree Fahrenheit.

coal, instead of in calories per gram. The latter expression multiplied by 1.8 gives the B. T. U. per pound. Consequently in the foregoing example

$$H = 6972 \times 1.8 = 12549.6 \text{ B. T. U. per pound.}$$

2. *The Determination of the Heating Value of Liquid and Gaseous Fuels*

The heating value of some liquid fuels may be determined by dropping the liquid on a small cellulose block¹ and then burning this in the usual manner in a bomb calorimeter. The determination is, however, customarily made with a calorimeter of the *continuous* type, such as that devised by Junkers. This instrument is primarily designed for use with gaseous fuels, but by means of special attachments it may be employed with liquid fuels as well.

The Junkers Gas Calorimeter

The calorimeter (Fig. 99) consists of an upright combustion chamber 28 through which the products of combustion from the flame 27 first rise, then pass downward through thin-walled copper tubes (shown in the cross section) and finally escape through 31 and 32. The rate of escape of these gases is controlled by the damper 33 and their temperature is shown by a thermometer inserted through an opening in the top of the pipe 32. The water vapor in the combustion gases is partially condensed and this condensed water flows out through 35. Cold water enters the apparatus at 3, passes downward through 6, rises around the bulb of the thermometer 13 and then enters the calorimeter and passes upward through the space around the heating tubes. At the top of the calorimeter the warmed water flows through the perforated plates 38 which have staggered holes to promote thorough mixing. It passes out of the apparatus through 18, 20 and 21 either to the measuring apparatus or to waste. The

¹ See Kellner, *Landwirtschaftl. Versuchsstat.*, 47 (1896), 275.

water is warmed in its passage through the calorimeter; the temperature of the inlet water is measured by the thermometer

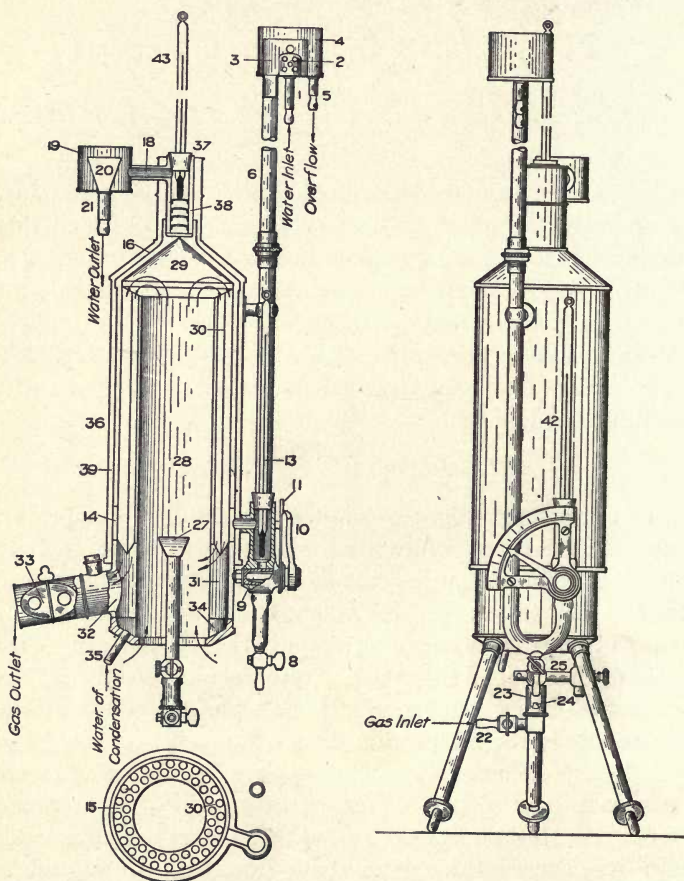


FIG. 99

13 and that of the escaping water by the thermometer 43. The calorimeter is surrounded by a polished nickel-plated jacket 36. The rate of the flow of the water is regulated by means of

the plug cock 9 and a pointer and scale shown in the figure to the right, and the head is kept constant by the overflow device 4. The rate of flow of the gas whose heating power is being determined is regulated by the cock 22.

The rate of flow of the water and the gas should be so adjusted that

(1) the escaping gases shall have approximately the same temperature as the surrounding atmosphere, and

(2) the difference in the temperatures of the entering water and the escaping water shall be from 5° to 10° , or sufficiently great to permit of accuracy in the heat calculations.

The determination of the heating power of a gas by the Junkers method is carried out as follows:

Preparation of Apparatus. — Level and adjust the experimental gas meter *G* (Fig. 100) and the pressure regulator at its right, and fill each with the proper amount of water. Connect them together with tubing and connect the inlet tube of the gas meter with the holder or main containing the gas to be examined. Attach the burner to the outlet tube of the pressure regulator by means of rubber tubing, place the burner on the table, turn on the gas and light it at the burner. Allow the gas to burn for about fifteen minutes to insure the saturation of the water in the meter and pressure regulator with the constituents of the gas mixture, and the removal of air from these instruments and from the connecting tube. In the meantime place the calorimeter in the position shown in the figure, and level it by means of the screws at the lower ends of the legs. The apparatus should be protected from drafts, and the temperature of the room should be as nearly constant as possible. Place the thermometers 13, 43 and 32, Fig. 99, in place and connect 3 with the water supply by means of a rubber tube. The entering water should have a temperature slightly lower than that of the room. Turn on the water, and by means of the pointer *E* adjust its rate of flow so that some of the entering water will overflow and pass out through 4 and 5.

Regulate the air supply to the burner to give a flame with a slightly luminous tip which will insure the perfect combustion of the entering gas and will prevent the cooling of the flame through an excess of air.

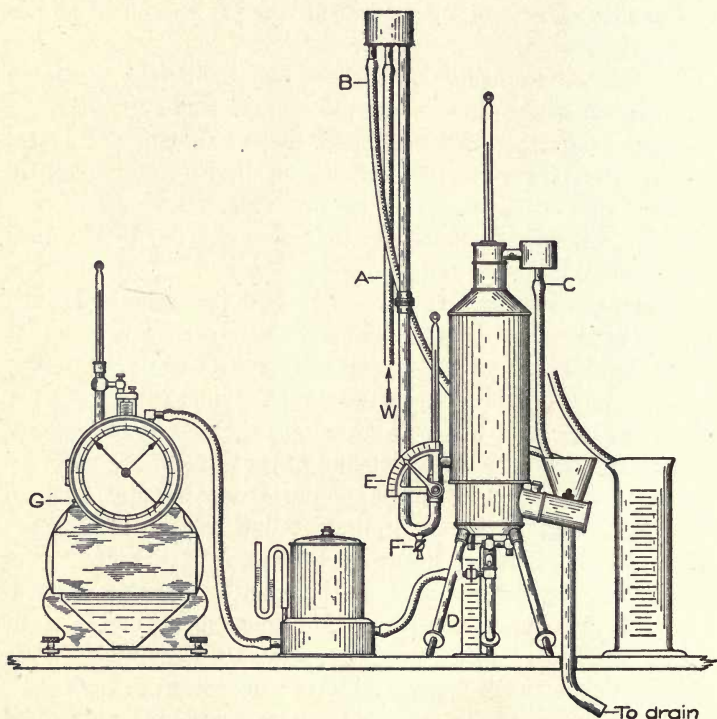


FIG. 100

Now insert the burner in the combustion chamber and screw it firmly into place in such position that the vertical tube will project about 12 cm. upward into the combustion chamber. A mirror held at an angle below the combustion chamber will enable the operator to see into the chamber and observe whether the burner is set in place in the middle of the chamber and whether the gas is burning properly.

Regulate the water supply by means of the pointer so that there is a difference of from 5° to 10° between the temperatures of the entering water and of that leaving the calorimeter. Read the thermometer inserted at 32 and note whether the escaping gases have approximately the temperature of the room. If they have not, adjust the rates of flow of the water and gas until this result is attained. When the temperatures of the escaping water and of the escaping gases have become constant and the condensed water has begun regularly to drop from the tube 35 the actual determination of the heating value may be begun.

Determination of the Heating Value of the Gas. — Read and record the prevailing barometric pressure, the temperature of the gas in the meter and the pressure of the gas on the manometer of the regulator. At the moment that the large hand of the gas meter passes the zero mark, note the position of the small hand of the meter and at once insert into the graduated cylinder of 2000 cc. capacity the rubber tube *C* that is connected with the outlet 21 and that has up to this time been connected with the drain. Place a 100 cc. graduated cylinder under the tube 35 to catch the condensed water. When the large graduated cylinder becomes filled to the upper mark it is replaced for the moment by a beaker and is emptied. It is then immediately returned to its position under the rubber tube and the water that has run into the beaker is poured into the cylinder. The number of times that the cylinder is emptied during the determination must, of course, be accurately recorded.

Read the thermometers 13 and 43 at one-half minute intervals. When from 30 to 50 liters of gas has been burned, note accurately the reading of the gas meter and at once remove the rubber tube from the large cylinder and withdraw the small cylinder in which the condensed water is being collected. Record the volume of water that has been measured in the large cylinder and the volume of the condensate that is collected in the small graduated cylinder. Again read the temperature of the gas in the me-

ter and the pressure that is shown on the manometer of the regulator. Then turn off the gas and after this has been done, shut off the water.

Calculation of Results. — Average the readings of the temperature of the gas in the meter and of the pressure on the manometer of the regulator at the beginning and the end of the experiment and use the mean values in the calculation of results.

Reduce the volume of gas that has been burned to the volume that it would occupy under standard conditions with the aid of the formula

$$v_0 = v \frac{p + s - m}{760 (1 + 0.00367 t)}$$

in which

v_0 represents the volume of the gas, in liters, under standard conditions,

v represents the volume of the gas, in liters, under the prevailing conditions,

p represents the barometric pressure in millimeters of mercury, s represents the reading of the manometer on the meter, in millimeters of mercury,

m represents the tension of water vapor at t° , in millimeters of mercury,

t represents the temperature of the gas in the meter.

The heat evolved by the combustion of the gas may be expressed as *total heat*, *gross heat*, or *net heat*.¹ Rosa defines *total heat* as the amount of heat measured by the calorimeter per unit quantity of gas burned, if the air (admitted to the calorimeter at room temperature) is dry, and if all of the water vapor formed by combustion is condensed in the calorimeter, and both it and the products of combustion escape at room temperature. *Gross heat* is the amount of heat measured by the calorimeter when the gas and the air are admitted to the calorimeter at room temperature, but are not dry, and when the products of combustion are cooled substantially to room temperature be-

¹ Rosa, The use of Gas for Heat and Power, *Centenary Celebration Lectures*, p. 143.

fore leaving the calorimeter, these products escaping as gases except for a small amount of water vapor that is condensed and collected as water at room temperature. The *net* heating value of a gas is the *total* heating value minus the latent heat at room temperature of all of the water vapor that is formed in the combustion.

The *gross heating value* of the gas may be calculated by means of the formula

$$H = \frac{WT}{V}$$

in which

H represents the heating value of the gas expressed in calories per liter,

W represents the number of cubic centimeters of water that has been heated,

T represents the average difference in the readings of the thermometers 13 and 43,

V represents the volume of gas in liters, under standard conditions, that has been burned.

The *net heating value* of the gas may be calculated by means of the formula

$$H' = \frac{WT - (637 - t) W'}{V}$$

in which

H' represents the lower heating value of the gas expressed in calories per liter,

W as above,

T as above,

V as above,

W' represents the number of cubic centimeters of water condensed during the combustion of the gas.

t represents the temperature of the condensed water escaping from 35, Fig. 99.

To express the heating power of a gas in B. T. U. per cubic foot, multiply the calories per liter by the factor 0.11236.

Gross and Net Heating Value. — A word of explanation as to the meaning of the terms *gross* and *net* heating value may not be out of place. When a gas that contains hydrogen or compounds of hydrogen is burned, steam is formed. If this steam at 100° is condensed to water at 100° within the heating apparatus, 537 calories are set free for every gram of water thus formed. This amount of heat thus becomes available and it, together with the heat liberated upon the cooling of the condensed water to room temperature, is included in the *gross* heating value of the gas.

When, however, the gas is used in gas stoves, gas engines or for the heating of Welsbach mantles, the steam that is formed is not condensed, and consequently its latent heat does not become available. Deduction of this loss gives the *net* heating value of the gas.

There is a considerable difference of opinion as to whether the *gross heating value* or the *net heating value* most accurately expresses the calorific power of the gas. A discussion of this question will be found in Stone's *Practical Testing of Gas and Gas Meters*.

Automatic Gas Calorimeter. — Professor Junkers has also devised an automatic form¹ of his calorimeter. The underlying principle of the device is the same as that employed in the other form of the Junkers apparatus, but the instrument is made automatic by rendering constant the ratio of the amount of gas burned to that of water passing through the calorimeter, in which case the difference of temperature is a direct measure of the heating value of the fuel. The temperature difference is measured by a thermocouple, the junctions of which are immersed in the entering and escaping water. The readings are made on a millivoltmeter.

¹ *J. Gasbeleuchtung*, 50 (1907), 520.

CHAPTER XVII

ACETYLENE GAS

The chief object of the analytical examination of acetylene is the detection and determination of certain impurities in the gas rather than the determination of acetylene itself.

Impurities in Commercial Acetylene.— Commercial calcium carbide may be contaminated with metallic calcium, calcium phosphide, calcium sulphide, aluminum carbide, aluminum nitride, magnesium nitride, or calcium nitride; consequently in the analysis of acetylene the following impurities have to be considered, — hydrogen, ammonia, phosphine, organic compounds of phosphorus, hydrogen sulphide, organic compounds of sulphur, silicon hydride, carbon monoxide,¹ methane (oxygen, nitrogen).

Of these, hydrogen, carbon monoxide, methane, oxygen, and nitrogen need not usually be determined since they are, as a rule, present in only small amounts, are without appreciable effect upon the luminosity of the acetylene flame, and, if they are susceptible of oxidation under the prevailing conditions, yield products that are not objectionable. On the other hand, ammonia, phosphine, organic compounds of phosphorus, hydrogen sulphide, organic compounds of sulphur, and silicon hydride should be tested for and, if found to be present, should be determined, because, upon combustion of the gas, nitric acid is formed from ammonia, phosphoric acid from phosphine and other compounds of phosphorus, sulphurous acid and sulphuric acid from hydrogen sulphide and other compounds of sulphur, and silicon dioxide from silicon hydride. These products of oxidation vitiate the air and attack or clog the metal parts of the burner.

¹ Keppeler, *J. Gasbeleuchtung*, 45 (1902), 804.

Sampling of Calcium Carbide. — The analyst may at times be called upon to analyze acetylene gas itself, but more often he is given a sample of calcium carbide and is asked to report upon the purity of the acetylene that is evolved from it. As commercial calcium carbide is usually far from uniform in composition, trustworthy results as to the purity of the acetylene that it yields can be obtained only from an average sample that is prepared from a fairly large amount of the carbide. Such a sample of the carbide cannot, however, be prepared in the usual manner by breaking the lumps into small pieces, grinding these to a powder, and mixing the powder. The substance is so hard that considerable time would be required to pulverize the pieces, and during the work the moisture of the air would decompose an appreciable amount of the carbide. The best that can be done under the circumstances is to rapidly break up the carbide into pieces about the size of a pea, to sift these without delay to remove the carbide dust, to then roughly mix the pieces of carbide together, and to place the material thus prepared in dry, tightly stoppered bottles. A sample prepared in this manner, is, of course, far from being homogeneous, and for this reason the portion of carbide taken for a determination should amount to about fifty, or even one hundred, grams.

Determination of Hydrogen in Acetylene. — Hydrogen in crude acetylene results from the action of metallic calcium upon the water used to decompose the calcium carbide, or from polymerization of acetylene and splitting off of hydrogen when the gas is generated at high temperature.

Hydrogen in acetylene may be determined with the Hempel apparatus by absorbing the acetylene with fuming sulphuric acid, oxygen with alkaline pyrogallol, the last traces of acetylene with ammoniacal cuprous chloride, and determining hydrogen (and methane if present) in the residue by combustion.

Determination of Ammonia in Acetylene. — Ammonia is formed by the action of water upon metallic nitrides, as



Lewes determines ammonia in crude acetylene by passing the gas through a solution of sulphuric acid of known strength and ascertaining the excess of sulphuric acid by titration of the solution with $\frac{N}{10}$ ammonium hydroxide, using litmus as indicator.

Determination of Phosphine in Acetylene. — Phosphine is almost always present ¹ in crude acetylene. It is due to the reaction between calcium phosphide and water. If the acetylene is evolved at high temperature, as is frequently the case when water is allowed to drop upon the calcium carbide, organic phosphorus compounds may also be formed, but if appreciable rise of temperature during the generation of the gas is avoided, the amount of these organic substances is negligible, and all of the phosphorus that is present may be assumed to exist in the form of phosphine.

The amount of phosphine in crude acetylene is quite variable, but it usually lies between .03 per cent and 1.8 per cent.² The regulations of the British Acetylene Association state that "carbide which, when properly decomposed, yields acetylene containing from all phosphorus compounds therein more than 0.05 per cent by volume of phosphine, may be refused by the buyer, and any carbide found to contain more than this figure, with a latitude of .01 per cent for the analysis, shall lie at the risk and expense of the seller. . . ." If the permissible maximum of phosphine lies in the neighborhood of .05 per cent by volume, it is apparent that the determination of this gas in crude acetylene cannot satisfactorily be accomplished by a volumetric absorption method that uses a sample of only one hundred cc. of acetylene.

Of the methods that have been proposed for the determination of the gaseous compounds of phosphorus in acetylene, the

¹ Vogel, *Handbuch für Acetylen*, p. 232.

² Vogel, *loc. cit.*, p. 234. The analyses given by Fraenkel, *J. Gasbeleuchtung*, 51 (1908), 431, show from .024 to .057 per cent by volume of phosphine in crude acetylene.

combustion method developed by Eitner,¹ Keppeler,² and Fraenkel,³ and the sodium hypochlorite absorption method of Lunge and Cedercreutz⁴ are in most general use. The first of these methods, in which the phosphorus in crude acetylene is determined by burning the gas and ascertaining the amount of phosphoric acid in the products of combustion, gives the total amount of phosphorus, whether it is present in the gas as phosphine or in the form of organic compounds of phosphorus. The acetylene is burned in an Acetylene-Bunsen burner under a cylindrical glass hood, and the products of combustion are drawn through an oxidizing solution, such as sodium hypochlorite or sodium hypobromite. The resulting phosphoric acid is then determined by precipitation with "magnesia mixture." On account of the difficulty in regulating the pressure of the gas as it comes from the evolution apparatus, Fraenkel recommends that the acetylene from about 50 grams of calcium carbide be collected over a salt solution in a large tubulated bottle, and that the gas be then driven from this bottle through the burner. This necessitates the use of glass bottles of about 20 liters capacity, and if the acetylene is to be mixed with an equal volume of hydrogen before combustion, as Fraenkel recommends, the containers must be so large as to render them very unwieldy and quite expensive. Moreover, the accuracy of the determination of phosphorus in the gas will undoubtedly be affected by the reaction between the compounds of phosphorus and the confining liquid.

For these reasons the method of Lunge and Cedercreutz in which the crude acetylene is passed directly from the generating apparatus through a solution of sodium hypochlorite is to be preferred to the combustion method if it will yield accurate results. The apparatus that was used by these authors is shown in Fig. 101. A weighed amount of the calcium carbide

¹ *J. f. Gasbeleuchtung*, **44** (1901), 548.

² *Ibid.*, **45** (1902), 802.

³ *Ibid.*, **51** (1908), 431.

⁴ *Z. f. angew. Chem.*, 1897, 651.

(from 50 to 70 grams) is placed in the flask *B*, and there is inserted into the neck of *B* a rubber stopper that carries a short delivery tube and a separatory funnel *A*. The ten-bulb absorption tube *C* is charged with about 75 cc. of a three per cent solution of sodium hypochlorite and is connected to the evolution flask. Water is now allowed to drop slowly from *A* upon the carbide in *B* at a rate of from 6 to 7 drops a minute. The evolution of acetylene will cease in from three to four hours.

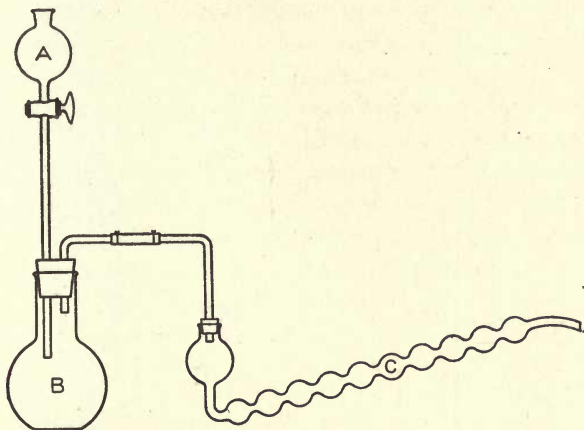


FIG. 101

Air is then drawn through the apparatus to carry over into *C* any acetylene that may still remain in *B*. The contents of the absorption tube *C* is transferred to a beaker and the phosphoric acid in the solution is precipitated by magnesia mixture.

Objection has been raised to this method because the acetylene is generated by dropping water upon calcium carbide, which is said to give rise to organic compounds of phosphorus that will pass through the solution of sodium hypochlorite without undergoing complete oxidation, and further because of the probable incompleteness of the absorption of the evolved phosphine by the solution of sodium hypochlorite in the ten-bulb tube.

In seeking to improve this absorption method two points that present themselves are, therefore,

(1) A method of generating acetylene that will avoid appreciable rise of temperature when the calcium carbide is decomposed, and

(2) An absorption apparatus that is more efficient than the ten-bulb tube used by Lunge and Cedercreutz.

The method described by Dennis and O'Brien¹ seems to fulfill these requirements in a most satisfactory manner.

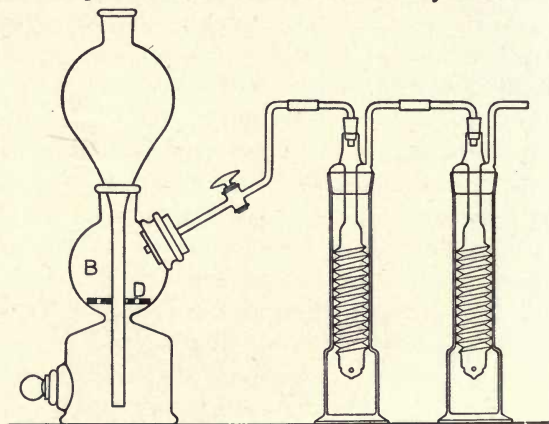


FIG. 102

The evolution of acetylene without marked rise of temperature is accomplished in simple fashion by the employment of a small Kipp apparatus about 40 cm. high, and with bulbs about 10 cm. in diameter. The annular space around the stem between the middle and bottom bulbs is covered with a perforated rubber disk *D* (Fig. 102). A solution of sodium chloride, saturated at room temperature, is poured into the top bulb until the end of the stem in the bottom bulb is covered with the liquid. A perforated stopper carrying a short glass tube is inserted in the neck of the top bulb, the stopper with exit tube and glass

¹ *Jour. Ind. Eng. Chem.*, 4 (1912), 834.

stopcock is inserted in the tubulus of the bulb *B*, and the further end of the outlet tube is connected with the absorption apparatus that contains the solution of sodium hypochlorite. Hydrogen gas is now passed into the upper bulb of the Kipp generator and through the absorption apparatus to displace the air. About 50 grams of the calcium carbide under examination, broken into pieces about the size of a pea and sifted to remove the dust, is placed in a dry weighing tube and this is at once tightly stoppered and weighed. When practically all of the air has been displaced from the Kipp apparatus by hydrogen, the stopper in the tubulus of the bulb *B* is removed, the contents of the sample tube is poured into the bulb and the stopper is at once reinserted. The current of hydrogen through the apparatus is continued for about one minute, the stopcock is then closed, and the stopper and tube are removed from the upper bulb of the Kipp generator. An additional amount of salt solution sufficient to cause the apparatus to function as a gas generator is then introduced into the upper bulb. The stopcock is now opened to such an extent that the evolved gases pass through the apparatus at a rate slightly faster than will permit of the bubbles being counted. Under these conditions the decomposition of a sample of 50 grams will be effected in about two hours. The reaction between the salt solution and the calcium carbide proceeds at a uniform rate, and with no appreciable rise of temperature.

The absorption apparatus that is employed is a Friedrichs gas washing bottle modified in form so that the apparatus can easily be rinsed out with water at the close of the run. The absorbing solution is introduced into the outer cylinder to such height that it will stand at the top of the widened foot of the cylinder, and the spiral with the ground glass shoulder is then inserted. When a gas is passed into the bottle through the central tube, it follows the grooves of the spiral when it rises and pushes some of the solution ahead of it. These gas washing bottles are much more compact than the ten-bulb tube

used by Lunge and Cedercreutz, and experiment has shown that the absorption attained by their use is surprisingly rapid and complete. The solution of sodium hypochlorite with which the absorption apparatus is charged is prepared by dissolving 15 grams of sodium hydroxide in 100 cc. of water, saturating the ice-cold solution with chlorine, driving out the excess of chlorine with a current of air, and then determining the amount of sodium hypochlorite in the solution by treatment with hydrogen dioxide in a Lunge nitrometer (see p. 397). The solution is then diluted to three per cent NaClO , and about 75 cc. of this solution is placed in each bottle.

After the decomposition of the calcium carbide is complete, the acetylene that remains in the generator is driven over into the absorption bottles by again passing hydrogen through the apparatus in the manner above described. The contents of the gas washing bottles is transferred to a beaker, the bottles and inner tubes being thoroughly rinsed with distilled water. 10 cc. of concentrated hydrochloric acid is added to the liquid which is then boiled until the odor of chlorine is no longer noticeable. Ammonium hydroxide is added to alkaline reaction and the phosphoric acid that is present is determined by precipitation with magnesia mixture, and weighing as magnesium pyrophosphate.

The volume of phosphine to which the weight of magnesium pyrophosphate is equivalent may be calculated as follows:—

$$\text{Mg}_2\text{P}_2\text{O}_7 : 2 \text{PH}_3 = 222.72 : 68.13,$$

or $\text{weight Mg}_2\text{P}_2\text{O}_7 \times 0.3059 = \text{weight phosphine}.$

Since one gram of phosphine occupies a volume of 657.9 cc. at 0°C . and 760 mm. pressure,

$$\begin{aligned} &\text{volume of PH}_3 \text{ in cc.} = \\ &\text{weight in grams Mg}_2\text{P}_2\text{O}_7 \times 0.3059 \times 657.9 \end{aligned}$$

or,

$$\begin{aligned} &\text{volume of PH}_3 \text{ in cc.} = \\ &\text{weight in grams Mg}_2\text{P}_2\text{O}_7 \times 201.25 \end{aligned}$$

Determination of Volume of Acetylene evolved from Sample of Carbide. — It is customary to report the results as the per cent by volume of phosphine in the evolved acetylene. This necessitates the determination of the volume of gas that is liberated by the calcium carbide under examination. The most convenient method for making this determination is that proposed by Bamberger¹ who places a definite amount of the carbide in a weighed two-neck Wolff bottle of about 400 cc. capacity, and runs in upon the carbide an amount of a saturated solution of sodium chloride sufficient to entirely decompose the substance. The whole apparatus is weighed before and after the reaction, and the loss in weight equals the weight of the evolved gas which is here assumed to consist entirely of acetylene. The total weight of the Bamberger apparatus before the decomposition of the carbide amounts to from 550 to 800 grams. This weight may materially be reduced by employing, in place of the Wolff bottle, an Erlenmeyer flask of about 250 cc. capacity. This is fitted with a two-hole rubber stopper into one opening of which is inserted the stem of a small separatory funnel of 125 cc. capacity; the other opening of the stopper carries a U-tube filled with calcium chloride. A sample of the calcium carbide amounting to about 50 grams is placed in a weighing bottle, is accurately weighed, and is then introduced into the flask. The stopper carrying the separatory funnel and the U-tube is then inserted, and the funnel is filled with a 20 per cent solution of sodium chloride. The whole apparatus is then weighed on a balance accurate to 0.01 gram. The total weight of this modified form of the Bamberger device is approximately 300 grams. The salt solution is now allowed to drop slowly upon the calcium carbide, and, after decomposition is complete, dry air is passed through the apparatus to expel all of the acetylene. The apparatus is then again weighed, the difference between the two weighings giving the weight of the acetylene evolved. One kilogram of chemically pure calcium

¹ *Z. f. Calc. und Acet.*, 1 (1898), 210.

carbide yields 405.93 grams of acetylene, equivalent to 348.4 liters of acetylene under standard conditions. Assuming that the loss of weight in the apparatus equals the weight of the acetylene evolved, the volume of the liberated gas may be calculated as follows:

Weight of sample : Weight C_2H_2 = 100 : x,

x = the weight of evolved acetylene expressed in per cent of weight of the calcium carbide.

Since *pure* calcium carbide will yield acetylene amounting to 40.593 per cent of the weight of the calcium carbide,

40.593 : per cent C_2H_2 by weight = 348.4 : x,

x = the number of liters of acetylene evolved from one kilogram of the calcium carbide under examination, or the number of cubic centimeters evolved from one gram of the carbide.

Calculation of Results.—From the above data the per cent by volume of the phosphine in the acetylene may now be calculated. An example of such a calculation follows:

A. Determination of Phosphine

Calcium carbide taken = 50.3548 grams.

Weight of $Mg_2P_2O_7$ = 0.0089 gram

cc. PH_3 from 1 gram CaC_2 = $\frac{0.0089 \times 201.25}{50.3548}$ = .035 cc.

B. Determination of Yield of Acetylene

Calcium carbide taken = 41.071 grams

Loss of weight of apparatus = 14.4885 grams

41.071 : 14.4885 = 100 : per cent C_2H_2 by wt.

Per cent C_2H_2 by weight = 35.28

40.593 : 35.28 = 348.4 : cc. C_2H_2 from 1 gram CaC_2

Volume C_2H_2 from 1 gram CaC_2 = 300 cc.

$$\begin{array}{l} \text{Per cent PH}_3 \\ \text{by volume} \end{array} = \frac{\text{cc. PH}_3 \text{ from 1 gram CaC}_2 \times 100}{\text{cc. C}_2\text{H}_2 \text{ from 1 gram CaC}_2} = 0.0117\%$$

To determine the accuracy of the results yielded by this method, it was necessary to ascertain

(1) Whether the gaseous compounds of phosphorus that are absorbed by sodium hypochlorite would be entirely taken up by two Friedrichs gas washing bottles containing the reagent, and

(2) Whether, in the method here employed for the generation of the acetylene, any gaseous compounds of phosphorus are evolved that are not absorbed by sodium hypochlorite.

That complete absorption of the compounds of phosphorus is obtained with only two of the gas washing bottles of the type here described, even when a sample of carbide unusually high in phosphorus was used, was demonstrated by connecting four of the absorption bottles in series, charging each with 75 cc. of a three per cent solution of sodium hypochlorite and testing the contents of each for phosphoric acid after the run. In no case was this acid detectable in the third or fourth bottle.

The second query was answered in two ways. The gases issuing from the second absorption bottle were burned with an excess of oxygen, and the products of combustion were found to be free from phosphoric acid. In another experiment the crude acetylene from the generator was burned directly without being passed through the solution of sodium hypochlorite, and the result was found to agree with that obtained by the absorption method.

The combustion of acetylene as it issues from a bottle containing a liquid absorbent has heretofore presented difficulty because of the intermittent flow of the gas. It was found, however, that complete combustion is easily attained by passing the acetylene into the hydrogen inlet tube of a Linnemann oxy-hydrogen lamp, admitting oxygen into the other tube of the lamp, and insuring continuous combustion by causing a small horizontal flame, about one cm. long, of illuminating gas

that is free from phosphorus to burn across the orifice of the lamp.

The accuracy and uniformity of the results obtained with the method here described are shown in the following tabulation of analyses by the absorption method, and by the method of combustion.

TABLE A

This sample CaC_2 yielded 300 liters C_2H_2 per kilogram

No.	Weight of sample in grams	Weight of $\text{Mg}_2\text{P}_2\text{O}_7$ in grams	PER CENT OF PHOSPHINE IN EVOLVED ACETYLENE	
			by NaClO method	by combustion method
1	50.3548	.0089	.0117	—
2	50.3572	.0073	.0097	—
3	50.1870	.0062	.0083	—
4	50.3027	.0050	.0066	—
5	50.0036	.0062	.0083	—
6	50.3047	.0059	.0078	—
7	50.1625	.0059	.0078	—
8	50.0000	.0072	—	.0096
9	50.0000	.0047	—	.0063
10	50.0000	.0060	—	.0080
11	50.0612	.0062	—	.0083
Average			.0086	.0080

TABLE B

This sample CaC_2 yielded 287 liters C_2H_2 per kilogram

No.	Weight of sample in grams	Weight of $\text{Mg}_2\text{P}_2\text{O}_7$ in grams	PER CENT OF PHOSPHINE IN EVOLVED ACETYLENE	
			by NaClO method	by combustion method
1	50.0651	.0661	.0925	—
2	50.0200	.0592	.0829	—
3	50.0432	.0782	.1093	—
4	50.1004	.0582	.0814	—
5	50.0600	.0680	—	.0948
6	50.1043	.0641	—	.0896
7	50.0612	.0601	—	.0841
8	50.0121	.0642	—	.0899
Average			.0915	.0896

The results given in Table A were obtained with a sample of commercial calcium carbide. To ascertain whether the method would give uniform results when the acetylene contained a relatively large amount of phosphine, a sample of calcium carbide high in phosphorus was prepared, and the analyses of this product by the two methods are given in Table B.

Determination of Sulphur in Acetylene. — The source of hydrogen sulphide in crude acetylene has been the subject of considerable discussion. It is commonly thought to be the calcium sulphide that is formed when the raw material from which the calcium carbide is prepared contains gypsum. But Moissan showed¹ that the product resulting from heating gypsum and carbon in an electric furnace gave with cold water an acetylene free from hydrogen sulphide, and moreover that the water used in the reaction after the residue had been removed by filtration gave no reaction for hydrogen sulphide. He therefore attributed the presence of hydrogen sulphide in crude acetylene to aluminum sulphide, which is easily decomposed by water with liberation of hydrogen sulphide.

In contradiction of this assumption, Wolff² found that samples of calcium carbide entirely free from aluminum liberated hydrogen sulphide when treated with water. When acetylene is set free from calcium carbide in such manner as to avoid appreciable rise in temperature, the evolved gas seldom contains hydrogen sulphide. It is known, however, that when calcium sulphide lies in contact with water for a considerable time, it changes to a soluble primary sulphide. It is reasonable to suppose that this change will take place more rapidly at high temperatures, and consequently when acetylene is set free by dropping water upon the carbide, hydrogen sulphide may result from the action of the water upon calcium sulphide. Moreover, Lunge and Cedercreutz found that crude acetylene contains

¹ *Compt. rend.*, 1898, 457.

² *Z. f. Calc. und Acet.*, 1 (1898), 272.

sulphur in a form not precipitable by lead acetate which indicated that the sulphur in the gas was in the form of organic compounds of the element. Caro considers¹ that these volatile organic sulphur compounds do not exist in the carbide, but are secondary products resulting from the action of hydrogen sulphide upon acetylene. Whatever their source may be, it is a fact that crude acetylene contains at times hydrogen sulphide and volatile organic compounds of sulphur, and consequently these substances must be taken into consideration in a complete analysis of the crude gas.

The determination of sulphur in acetylene may conveniently be combined with the determination of phosphine (see under Phosphine, p. 360). The sodium hypochlorite solution oxidizes compounds of sulphur to sulphuric acid. Phosphoric acid that is simultaneously formed is precipitated by magnesia mixture that is free from sulphates. After the ammonium magnesium phosphate precipitate has been removed by filtration, the filtrate is acidified with hydrochloric acid, heated nearly to boiling, and the sulphuric acid precipitated with barium chloride. It has been claimed by some that this method does not oxidize all of the sulphur compounds in the gas, and that accurate results will be obtained only when the crude acetylene is burned and the sulphuric acid is determined in the combustion products.

Determination of Silicon Hydride in Acetylene. — There is considerable difference of opinion as to whether this gas is present in acetylene. The work of Lewes and of Fraenkel appears to demonstrate its existence in certain samples of crude acetylene although the amounts that they found were quite small, about 0.01 per cent by volume or ten cc. in 100 liters. The gas may be determined by the method used by Fraenkel² which consists in burning crude acetylene under a cylinder of glass, or better of platinum, rinsing out the cylinder with hy-

¹ *Z. f. Calc. und Acet.*, 1 (1898), 337.

² *J. f. Gasbeleuchtung*, 51 (1908), 433.

drochloric acid and determining the silica that has resulted from the combustion.

Determination of Carbon Monoxide in Acetylene.—Kepeler¹ believes that crude acetylene contains a small amount of carbon monoxide and bases his belief upon the fact that after he had absorbed the acetylene by fuming sulphuric acid in a Hempel pipette and had treated the gas residue with potassium hydroxide, bromine and phosphorus, there was further absorption when the residual gas was passing into a pipette containing a solution of cuprous chloride. Assuming that this absorption was due entirely to carbon monoxide, he found that the amount of that gas was about 0.02 per cent of the crude acetylene.

Lundström,² however, found as much as 1.48 per cent of carbon monoxide in acetylene, and Caro as high as 2.3 per cent. The source of the carbon monoxide is still in doubt.

Determination of Methane in Acetylene.—From the work of Rossel and Sandriset³ and of v. Knorre and Arndt,⁴ it would appear that there is no methane in acetylene that has been properly generated. If, however, the gas is evolved at high temperature, it may contain considerable amounts of methane.⁵ The gas may be determined, together with any hydrogen that may be present in the acetylene, by combustion of the non-absorbable residue (see under Hydrogen, p. 356).

Determination of Oxygen and Nitrogen in Acetylene.—Oxygen and nitrogen may be determined volumetrically by the procedure described under hydrogen, p. 356, the nitrogen being the gas that remains after the determination of hydrogen and methane.

¹ *J. f. Gasbeleuchtung*, **45** (1902), 802.

² *Chemiker-Zeitung*, **23** (1899), 180.

³ *Z. f. angew. Chem.*, 1901, 77.

⁴ *Z. d. Ver. z. Förderg. d. Gewerbeleisses*, 1900, 162.

⁵ *Lewes, J. Soc. Chem. Ind.*, **17** (1898), 533.

CHAPTER XVIII

EXAMINATION OF ATMOSPHERIC AIR

Composition of Atmospheric Air. — The normal constituents of the atmosphere are nitrogen, oxygen, the gases of the argon group, carbon dioxide and water vapor. These substances, with the exception of water vapor, are present in nearly constant amount in air that is free from local contamination.

Nitrogen	78.1	per cent by volume
Oxygen	20.94	" "
Carbon Dioxide	0.03	" "

Argon	1 volume in	106.8 volumes of air
Neon	1 " "	80,800 " "
Helium	1 " "	245,300 " "
Krypton	1 " "	20,000,000 " "
Xenon	1 " "	170,000,000 " "

Local conditions may, however, give rise to the presence in air of such substances as ammonia, nitrous acid, nitric acid, sulphur dioxide, sulphuric acid, carbon monoxide, soot, ozone,¹ etc. The possibility of the presence of these and other occasional constituents in the atmosphere renders it necessary to adopt such methods in the examination of air as will meet the demands of the special case in hand. The determination of most of the substances enumerated above is discussed in Chapter XIII. Two constituents, however, water vapor and carbon dioxide, deserve special consideration because almost every examination of air from a sanitary standpoint involves the determination of these two substances. Many methods for rapidly and accurately determining these constituents of the atmosphere have been de-

¹ See p. 178.

veloped, and a few of the more satisfactory procedures thus far devised will here be described.

A very complete discussion of the history of air analysis, and of the amounts of oxygen and carbon dioxide in the atmosphere has recently appeared from the pen of F. G. Benedict.¹

DETERMINATION OF MOISTURE IN THE ATMOSPHERE

Absolute and Relative Humidity. — Water vapor is always present in atmospheric air, but the amount varies greatly. The maximum quantity of water vapor that can be present in any given space is dependent upon the prevailing temperature but is independent of the amount of air in that space. When this maximum quantity of water vapor is present, the space is said to be saturated with water vapor. The quantity of water vapor existent in a given space, such as a cubic foot or a cubic meter, is termed the “absolute humidity” and may be expressed in terms of its weight (in grains or grams) or of its pressure (in inches or millimeters of mercury). The ratio between the amount of water vapor actually present in a given space and the maximum quantity of the vapor that could exist in that space at the observed temperature is termed the “relative humidity.” It is usually expressed in per cent of the maximum humidity.

Wet and Dry Bulb Thermometers. — Of the large number of methods that have been devised for the determination of the amount of water vapor in air, one of the most satisfactory is that employed by the Weather Bureau of the United States Department of Agriculture. It is based upon the facts that water will evaporate as long as the adjacent space is not saturated with water vapor, and that this evaporation is accompanied by the absorption of heat. Consequently, if two thermometers are exposed to the air and a moist cloth is placed around the bulb of one of them, this “wet bulb” thermometer will show a

¹ *The Composition of the Atmosphere.* Publication No. 166 of the Carnegie Institution of Washington, 1912.

lower temperature than the "dry bulb" thermometer unless the surrounding space is saturated with water vapor. The less the amount of moisture in the air, the greater will be the drop in temperature of the wet-bulb thermometer. From the final

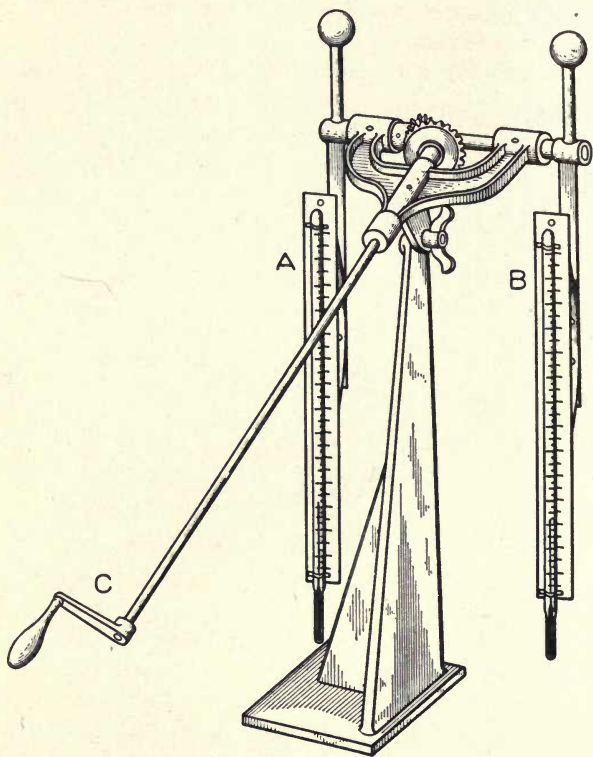


FIG. 103

readings of the two thermometers the amount of water vapor then present in the air may be calculated.

The Whirling Psychrometer. — The instrument employed by the Weather Bureau for this work is termed the *whirling psychrometer*. Fig. 103. It consists of two thermometers *A* and *B*

which are mounted upon arms that can be whirled by turning the handle *C*. The bulb of one thermometer (the "wet bulb") is covered with a piece of thin muslin that should first be washed to remove sizing. A small rectangular piece of the washed muslin, wide enough to go about one and one-third times around the bulb, and long enough to cover the bulb and a part of the stem above the bulb, is thoroughly moistened with distilled water and is neatly fitted around the thermometer. It is first tied around the upper end with a piece of strong thread. A loop of thread is next passed around the lower end where it projects beyond the bulb, and the thread is then drawn tightly around the muslin in a knot close up to the lower surface of the bulb and the knot is secured. If this is properly done the muslin will be neatly stretched over the bulb and securely fastened at the bottom.¹

Manipulation of the Whirling Psychrometer.—In making a determination of atmospheric moisture the "wet bulb" is dipped into a cup of pure water to thoroughly saturate the muslin with water. The handle *C* is then turned and the thermometers are rapidly whirled for from fifteen to twenty seconds. The whirling is stopped, and the two thermometers are quickly read, the "wet bulb" thermometer being first read. They are immediately whirled again and a second reading is taken. This is repeated until two successive readings of the "wet bulb" agree very closely, which shows that the thermometer has reached its lowest temperature. The thermometers must usually be whirled a minute or more before this temperature is reached.

The rate of evaporation of the water surrounding the "wet bulb" will vary as the movement of the air past the bulb varies, and for these reasons accurate results cannot be obtained unless the speed of passage of the air by the bulb is rapid and uniform. It is for this reason that the thermometers are whirled. The whirling should not be too fast, but should be carried on at such rate that the bulb of the thermometer will have a veloc-

¹ See U. S. Dept. of Agriculture, *Weather Bureau, Bulletin No. 235*, p. 5.

ity of about fifteen feet per second, which with the above instrument will be obtained by turning the handle *C* about one and one-half revolutions per second.

Calculation of Results. — In the calculation of results the following equation is employed:

$$e = e' - 0.000367 P (t - t') \left(1 + \frac{t' - 32}{1571} \right)$$

in which *e* is the absolute humidity in inches of mercury, *t* and *t'* are the temperatures respectively of the "dry" and "wet bulb" thermometers expressed in degrees Fahrenheit, *P* is the barometric pressure of the air in inches of mercury and *e'* is the maximum tension of water vapor in inches of mercury at the temperature *t'* of the "wet bulb."

The relative humidity may then be calculated with the aid of the tables given in the bulletin of the Weather Bureau cited above.

It would seem preferable, in scientific work, to express the temperatures in degrees Centigrade, and the barometric pressure in millimeters of mercury. If this be done the formula becomes

$$e = e' - .000661 B (t - t') \frac{(873 + t')}{873}$$

in which *B* is the barometric pressure in millimeters of mercury, and *t* and *t'* are the temperatures of the wet and dry bulb thermometers in degrees Centigrade.

The absolute humidity *e* having thus been ascertained, the *relative humidity* is calculated by dividing this result by the maximum tension of water vapor *E* possible at the temperature shown by the dry bulb thermometer. This result multiplied by 100 gives the relative humidity expressed in "degrees" or per cent.

$$\begin{array}{l} \text{Relative humidity in} \\ \text{degrees or per cent} \end{array} = \frac{e}{E} \times 100$$

The values of E at temperatures between -2°C. and $+34^{\circ}\text{C.}$ will be found on p. 411.

The August Psychrometer.—A somewhat simpler instrument than the whirling psychrometer but one that is based upon the same principle is the August Psychrometer. It consists of two thermometers placed side by side on a stand. The bulb of one of the thermometers is covered with thin muslin that is kept moist by a small lamp-wick which is fastened over the muslin and dips into a vessel that contains water. Evaporation is allowed to proceed until the temperature of the wet bulb ceases to fall. The temperature of this thermometer, t' , is then read, and also that of the dry thermometer, t . The absolute humidity of the air is then calculated with the use of the formula —

$$e = e' - k (t - t') b$$

in which e' is the tension corresponding to the temperature t' , and b is the barometric pressure in millimeters. k is an empirical factor that varies with the speed of flow of the air past the wet bulb. According to the researches of Regnault, the values for k under different conditions are as follows: —

In small closed rooms	0.00128
“ large “ “	0.00100
“ halls with open windows	0.00077
“ courts	0.00074
“ open air (no wind)	0.00090

It is not always easy, however, to decide which factor should be used, and experience has shown that the August psychrometer will yield satisfactory results only when it is standardized against the whirling psychrometer, and the proper factor for the special surroundings is thus determined.

The Hygrodeik.—There is obtainable on the market a convenient modification of the August psychrometer that is termed Lloyd's Hygrodeik. By means of a pointer and chart attached to this instrument, the relative humidity of the atmosphere may be read off with ease and celerity.

Determination of Carbon Dioxide in the Atmosphere

The deleterious effects that result from the breathing of air in crowded or ill-ventilated rooms have, until quite recently, been supposed to be due to poisonous substances exhaled from the lungs of the occupants. Inasmuch as it has been impossible to ascertain the quantity of these emanations from the lungs, the carbon dioxide, which is simultaneously exhaled and which can be accurately determined, has been regarded as a measure of the toxic organic substances.

The theory is now advanced that the injurious effects arising from poor ventilation are due not to toxic emanations from the lungs, but rather "to a disturbance of the normal thermal relations of the body. It is a common observation that the depression and fatigue experienced on a hot, humid August day are very similar to the feelings that develop in a crowded 'close' room. The cause is apparently the same in both cases, namely, interference with the normal rate of loss of body heat. At least three atmospheric factors may be concerned in such interference: high temperature of the ambient air, high moisture content and lack of air movement. Paul¹ kept healthy persons for several hours in a close cabinet until the carbon dioxide rose to 100 or 150 parts per thousand — more than ten times the amount usually stated as 'allowable' — but so long as the temperature and moisture content were kept low, no symptoms of illness or discomfort developed. Other experimenters have reached the same result by simply having electric fans whirled in such an experiment cabinet. The motion these imparted to the air was sufficient to facilitate a normal, physiologic loss of heat from the body in spite of high temperature and humidity. Similar cabinet experiments in which the subject was enabled to breathe the fresh outside air through a tube, but was otherwise subjected to the conditions of a close room,

¹ Paul, *Ztschr. f. Hyg.*, 49 (1905), 405.

likewise showed that the symptoms attributed to 'bad ventilation' are in nowise due to poisons excreted in the breath. The upshot of all such experiments is that it is not the chemical constitution of indoor air that is injurious, but the overheating, the stagnation and sometimes the moisture content."¹

Even if this view were correct, it still remains true that the amount of carbon dioxide in the air of a room furnishes a means of judging the efficiency of the ventilation, and for this reason the accurate determination of this constituent is still of importance even although it should appear that the accompanying exhaled products from the lungs are not toxic in character.

According to Benedict ² the amount of carbon dioxide in air serves as quite an exact indication of the per cent of oxygen that is present. "For every 0.01 per cent increase in the atmospheric carbon dioxide, one may safely assume a corresponding decrease in the percentage of oxygen."

Methods employed in Determination of Carbon Dioxide in Air. — The methods that have been devised for the determination of carbon dioxide in the atmosphere may roughly be divided into two classes — those in which the carbon dioxide is absorbed by a suitable solution of known strength, and the excess of the absorbent is determined by chemical means, and those in which the carbon dioxide is absorbed and the consequent decrease in the volume of the sample of air is measured.

The Hesse Method. — A great number of methods of the first class have been proposed. Most of them aim to give approximate results in a short space of time. These will not here be considered. Of the other and more accurate methods, that original with Saussure and improved by Pettenkofer and later by Hesse ³ has proven itself to be one of the most satisfactory.

¹ *Jour. Amer. Med. Association*, September 16, 1911, Vol. 57, No. 12, p. 980.

² *The Composition of the Atmosphere*. Publication No. 166 of the Carnegie Institution of Washington, 1912, p. 115.

³ *Anleitung zur Bestimmung der Kohlensäure in der Luft, nebst einer Beschreibung des hierzu nöthigen Apparates*; Eulenberg's *Vierteljahrsschr. f. gerichtl. Medicin und öffentl. Sanitätswesen*, N. F. 31, 2.

In this procedure the carbon dioxide in a known volume of air is absorbed by a solution of barium hydroxide of known strength and the amount of barium hydroxide that has not combined with carbon dioxide is then determined by titration with a solution of oxalic acid, phenolphthalein being used as indicator.

Solutions used in the Hesse Method. — The stock solutions needed in the analysis are the following —

(1) One kilogram of barium hydroxide and 50 grams of barium chloride are added to about five liters of distilled water contained in a large bottle. As the clear supernatant liquid is used, it is replaced by water so long as there is solid material in excess.

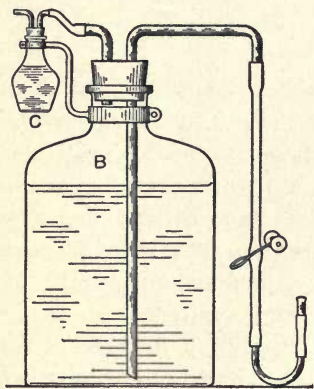


FIG. 104

(2) A dilute solution of barium hydroxide that is prepared by adding about 30 cc. of the concentrated solution No. 1 to one liter of water. This is placed in a bottle *B* (Fig. 104), provided with a small absorption bottle *C* that contains potassium hydroxide which frees the entering air from carbon dioxide. This dilute solution may also be prepared directly by dissolving 1.7 grams of a mixture of barium hydroxide and barium chloride (20:1) in one liter of distilled water. Phenol-

phthalein is added to this solution until it has a faint but distinct pink color.

(3) A solution of oxalic acid that contains 5.6325 grams of crystallized oxalic acid in one liter of water. One cc. of this solution is equivalent to one cc. of carbon dioxide.

(4) A solution of phenolphthalein that contains one part of the substance dissolved in 250 parts of alcohol.

Collection of Samples of Air. — The samples of air are collected in thick-walled Erlenmeyer flasks of 100, 200, 300, 400, 500 cc. capacity that are supplied with tightly fitting, double-bore rubber stoppers. The point to which the rubber stopper reaches into the neck of the flask is marked on each flask, and the capacity of the flask up to this line is determined and is marked on the glass. Pieces of glass rod from 3 to 5 cm. long are used to close the openings in the stoppers. These rods should be well rounded at the lower ends and should be widened at the upper end by heating them in the flame of a blast lamp and pressing them on a cold surface. Further apparatus that is needed in the work comprises a pipette of 10 cc. capacity, and a burette with glass stopcock. The burette has a capacity of from 10 to 15 cc., is graduated in $\frac{1}{10}$ cc., and has a tip about 8 cm. long.

Manipulation. — Each determination of carbon dioxide by Hesse's method is in reality a double one, two determinations of the constituent being made in samples of air of different volumes. These samples are collected in two of the Erlenmeyer flasks above described, the two flasks being of different capacity and the sizes of the flasks that are used depending upon whether a smaller or a larger amount of carbon dioxide in the air is to be expected. The samples of air are collected by completely filling the flasks, at the place where the air is to be examined, with distilled water that has the same temperature as the surrounding air, and then pouring out the water and immediately inserting the rubber stoppers in the necks of the flasks, the holes of the stoppers being closed with the glass plugs. In this operation care should be exercised that the flask is not warmed by the hand and that no air exhaled by the operator enters the flask. The flasks are transferred to the laboratory and the carbon dioxide in each of the two samples is then determined. The glass plug is removed from the end of the rubber tube (Fig. 104), the tip of the 10 cc. pipette is inserted into the end of the tube, the

pinchcock is opened and some of the solution of barium hydroxide is drawn up into the pipette. The pipette is rinsed with this solution which is then driven out of the pipette. The pipette is then reinserted in the end of the rubber tube and barium hydroxide is drawn up to the zero mark whereupon the pinchcock is closed. One of the glass plugs in the stopper of one of the Erlenmeyer sample flasks is withdrawn and the tip of the pipette is inserted into the flask through this opening. The solution of barium hydroxide is then run into the flask, the air that is displaced by the solution being allowed to escape by momentarily removing the glass plug in the other hole of the stopper. The last drops of barium hydroxide in the pipette are driven out by closing the upper end of the pipette with the finger, and warming the wider portion of the pipette with the hand. The pipette is then withdrawn from the flask and the stopper is closed with the glass plug. This procedure is repeated with the other sample of air contained in the second flask. The closed flasks are allowed to stand for from fifteen to twenty minutes with occasional shaking. For the complete absorption of the carbon dioxide in the sample of air in the flask it is essential that the barium hydroxide be present in so large excess that not more than one-fifth of it enters into the reaction. If the sample of air is quite large, or if the carbon dioxide contained is high, 20 or even 25 cc. of the solution of barium hydroxide should be used.

While the absorption of carbon dioxide in the flask is proceeding, the strength of the solution of barium hydroxide is determined by filling the burette to the mark with the dilute, standardized solution of oxalic acid (0.56325 gram per liter), inserting the tip of the burette through one opening of a two-hole rubber stopper, placing the stopper in the neck of a 100 cc. Erlenmeyer flask in the manner shown in Fig. 105, and then running into the flask a volume of the solution of oxalic acid almost sufficient to neutralize 10 cc. of the solution of barium hydroxide. 10 cc. of this latter solution is

then introduced into the flask in the manner above described and the oxalic acid is then carefully added until the pink color of the indicator just disappears. This color will frequently reappear on standing because of the presence of traces of potassium hydroxide or sodium hydroxide in the solution.

The excess of barium hydroxide in the two sample flasks is then titrated by filling the burette to the mark with the standardized, dilute oxalic acid, inserting the tip of the burette through one of the openings of the stopper and running in the oxalic acid at first rapidly, and then toward the end of the reaction drop by drop. The increase of pressure in the flask is relieved from time to time by momentarily lifting the glass plug in the other opening of the stopper. As before, the end point of the reaction is the first disappearance of the pink color.

Calculation of Results. — The temperature and the prevailing atmospheric pressure are then read.

10 cc. is deducted from the volume of each sample flask to allow for the volume of air displaced by the solution of barium hydroxide that has been introduced, and the remaining volume is corrected to standard conditions of temperature and pressure. This result represents the volume of the air sample in the flask. The number of cubic centimeters of the solution of oxalic acid required to neutralize the excess of the barium hydroxide is deducted from the volume of oxalic acid required to neutralize 10 cc. of the barium hydroxide. Representing this difference by n , the amount of carbon

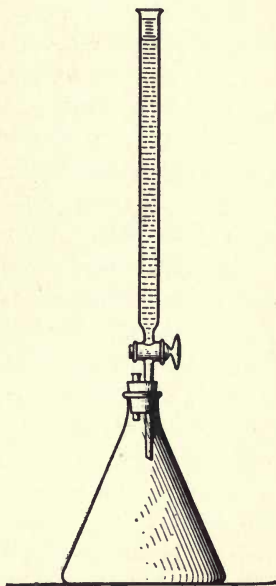


FIG. 105

dioxide in the sample may be calculated by means of the following proportion:

$$\frac{n}{10} : \text{volume of air sample taken} = x : 10,000$$

in which x represents the parts of carbon dioxide per 10,000 of air.

The Pettersson-Palmqvist Method. — Of the second type of methods for the determination of small percentages of carbon dioxide, that devised by Pettersson and Palmqvist ¹ is one of the most satisfactory and accurate.

The apparatus that they designed permits of the measurement of as small a volume of air as 25 cc. with an accuracy of one part in 10,000, and avoids the necessity of making corrections for variations in pressure and temperature. This is made possible by the use of a compensating tube that is filled with air and that stands in communication with one side of a manometer tube, the burette in which the air is measured being attached to the other side of the manometer. Both compensating tube and burette, which are of nearly the same capacity, stand in a vessel of water. If the temperature of this surrounding water changes during the experiment the effect upon the volume of air in each tube is the same.

If, now, the two tubes are always brought into communication with the manometer when the air in the burette is measured, it follows that if the liquid in the manometer is brought to the same point in each case, the air in the burette is measured under exactly the same conditions of pressure and temperature as prevail in the compensating tube, and since the inclosed volume of air in the compensating tube, which is of course unaffected by changes in barometric pressure, is at each measurement brought back to the volume corresponding to the original conditions of temperature and pressure, the air in the burette is similarly affected, and for this reason no corrections for changes in temperature and pressure are necessary.

The apparatus of Pettersson and Palmqvist, with slight

¹ *Berichte der deutschen chemischen Gesellschaft*, 20 (1887), 2129.

modifications introduced by the author, is shown in Fig. 106. The air is measured in the burette *A* which contains 25 cc. from a mark on its upper capillary tube down to the zero point at the lower end of the capillary *S*. This capillary is calibrated in divisions each of which amounts to $\frac{1}{10,000}$ part of the total volume of the burette. The somewhat wider capillary *T* is calibrated in divisions that represent $\frac{1}{1,000}$ part of the volume of the burette. The lower end of *T* is connected by means of a piece of rubber tubing with the glass stopcock *V*; this rubber tube can be compressed by turning the screw *N* and forcing down upon the tube a flat metal plate attached to the end of the screw. The lower tube of the stopcock *V* is joined to the level-bulb *E* by a piece of enamelled rubber tubing. At the upper end of the burette *A* are three branch capillary tubes. The one to the left in the drawing is provided with the two-way stopcock *J* through which the sample of air is drawn into the apparatus either directly from the outer atmosphere through *P* or through the coil of copper tubing *H* and the glass tube *I*. At the right, *A* is connected through the stopcock *L* with an Orsat gas pipette *B* that contains glass tubes and is charged with a solution of potassium hydroxide for the absorption of carbon dioxide. The other branch capillary tube joins *A* through the stopcock *K* to the manometer *M* which may be brought into communication with the outer air by opening the stopcocks *F* and *G*. The other end of *M* is connected by the rubber tube *D* to the glass compensating tube *C*. The burette *A*, the pipette *B*, the compensating tube *C* and the coil of copper tube *H* as well as the capillary tubes *S* and *T* are surrounded by water that is contained in the wide glass cylinder and in the jacket tube around the lower capillaries. The whole apparatus is mounted on a board about 90 cm. high and 30 cm. wide which is itself set into a square wooden base. The apparatus can be covered by a wooden box that slides down over it and that is held in place by the screws shown at the top of the board. This cover does not appear in the figure.

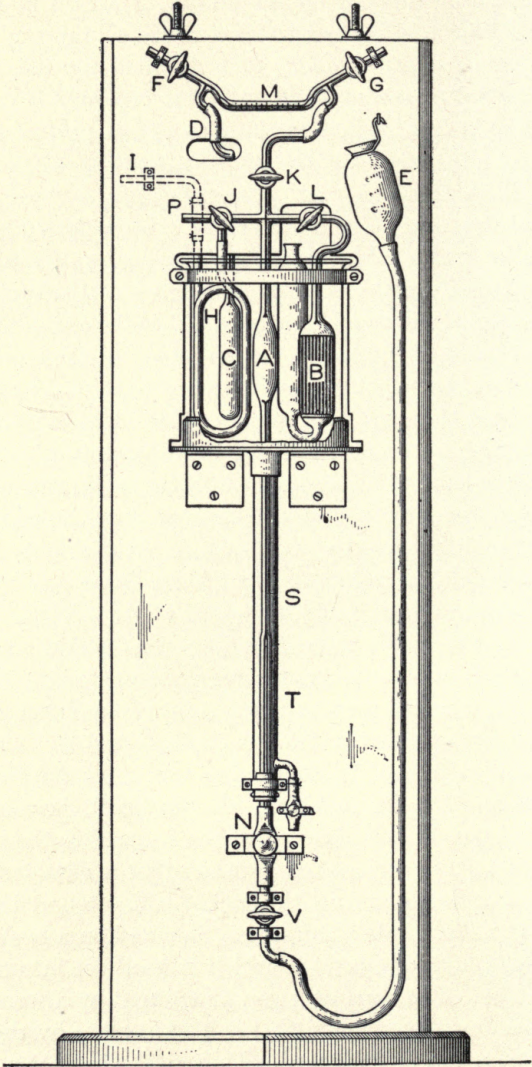


FIG. 106

The manometer *M* contains a drop of petroleum in which azobenzene is dissolved and there is etched upon the surface of the tube a scale by means of which the position of the drop may be read.

The coil of copper tube *H* has been added to the original Pettersson-Palmqvist apparatus because it has been found, in determining the carbon dioxide in the air of rooms that are or recently have been occupied, that it takes several minutes for the sample of warm air from the upper part of the room to fall to the temperature of the water that surrounds *A*. This is shown by the side movement of the drop of liquid in the manometer after the sample has been measured. If, however, instead of drawing the air directly into *A* through *P* it is caused to pass through the coil *H*, which is about 80 cm. long, 3 mm. internal diameter, and 5 mm. external diameter, the entering sample of air is rapidly cooled (or warmed) to the temperature of the surrounding water.

It has oftentimes been noticed that the change in the volume of the sample of air in *A* that is caused by its rising or falling to the temperature of the surrounding water, produces a greater movement of the manometer liquid than would result from the removal of the carbon dioxide in the sample.

In making a determination of carbon dioxide with this apparatus, clean mercury is poured into the level-bulb *E* in an amount sufficient to fill the connecting tubes and the burette *A*. The stopcock *J* is turned to such position that *A* communicates with *P*, and one drop of water is introduced into the end of the tube and is drawn over into *A*. The absorption tube *B* is then filled with a 33 per cent solution of potassium hydroxide. The apparatus is now transferred to the place where the air or other gas mixture is to be examined. The glass cylinder surrounding the absorption and measuring tubes is filled with water of the temperature of the surrounding air. Stopcocks *V* and *J* are now opened, the level-bulb *E* is raised, and mercury is driven nearly to the top of the burette *A*. *J* is now closed, the level-

bulb *E* is lowered, the stopcock *L* is carefully opened, and the solution of potassium hydroxide in the absorption tube *B* is drawn up to a mark on the stem at which this solution must always stand when measurements are made. *L* is then closed, *J* is turned to such position that *A* communicates with *P* and the mercury in the burette *A* is raised until it stands at the mark on the capillary tube above the burette. The level-bulb *E* is now slowly lowered, and air is drawn into *A* until the mercury falls to about the point *T*. *J* is then turned to such position that *A* communicates with the coil *H* and the level-bulb is now raised and this first sample of air is driven out through the outlet *I*. A second sample is now drawn in through *I* and *H* by lowering *E*, the mercury being allowed to fall to a point slightly below the zero mark on the capillary tube *S*. The stopcocks *J* and *V* are then closed and the rubber tube at the bottom of the measuring burette is compressed by turning the screw *N* until the mercury stands exactly at the zero mark of the tube *S*. The stopcock *J* is then opened for a moment to bring the sample in the burette *A* to atmospheric pressure. The stopcocks *F* and *G* are next carefully opened to bring the air upon both sides of the manometer and in the compensating tube *C* to atmospheric pressure. In this operation care must be exercised to avoid driving out the drop of liquid from the tube *M*. *F* and *G* are now closed, the stopcock *K* is carefully opened, and the position of the drop of liquid in the manometer *M* is noted. The stopcock *K* is then closed, the stopcocks *V* and then *L* are opened, and the sample of air is driven over into the absorption pipette *B* where it is allowed to remain for one minute in contact with the absorbent. The level-bulb *E* is then lowered and the solution of potassium hydroxide in *B* is drawn up again to the mark, whereupon *L* is closed. The residual gas in the burette *A* is now brought approximately to atmospheric pressure by proper adjustment of the height of the level-bulb *E* and the stopcock *V* is then closed. *K* is opened and the drop of liquid in the manometer *M* is brought to its original position by turning the com-

pression screw *N*. The final volume of the gas is now read off on the capillary tube *S* and the difference between this reading and the reading of the initial volume, expressed in divisions on this tube, corresponds to the parts of carbon dioxide per 10,000 in the sample of air under examination.

If the carbon dioxide in the sample is higher than 0.4 per cent, the wider calibrated capillary tube *T* is employed in making the measurements, one division on this tube corresponding to one part of carbon dioxide per 1,000 parts of air.

A serious objection to the Pettersson-Palmqvist apparatus is its size and weight. It is also quite difficult to replace any of the glass parts that may be broken. Modifications of the apparatus, with a view to making it more easily portable, have been proposed by Bleier¹ and Rogers, but in the opinion of the author, the objections to the original form are most satisfactorily met by the device described by Anderson² and shown in Fig. 107.

Anderson's Modification of the Pettersson-Palmqvist Apparatus. — The gas is measured in the burette *A* and the change in volume of the sample that results when the carbon dioxide is absorbed is read upon the capillary *S*. This bent capillary tube passes through a stopper and is joined to the stopcock *V* by a piece of rubber tubing. This rubber tube passes under the compression screw *N* by means of which the fine adjustment of the mercury in the capillary tube *S* is effected. The other side of the stopcock *V* is connected with the level-bulb *E* by a piece of enamelled rubber tubing. A solution of potassium hydroxide for the absorption of carbon dioxide is contained in the pipette *B*, *C* is the compensating tube, and *M* the manometer. By means of the three-way stopcock *J* the sample of air may be drawn through the coil of copper tubing *H*, *H'*, *H''*. The compensating tube *C* may, by means of the three-way stopcock *F*, be brought into communication with the

¹ *Z. f. Hygiene*, 27 (1898), 111.

² *J. Amer. Chem. Soc.* 35 (1913), 162.

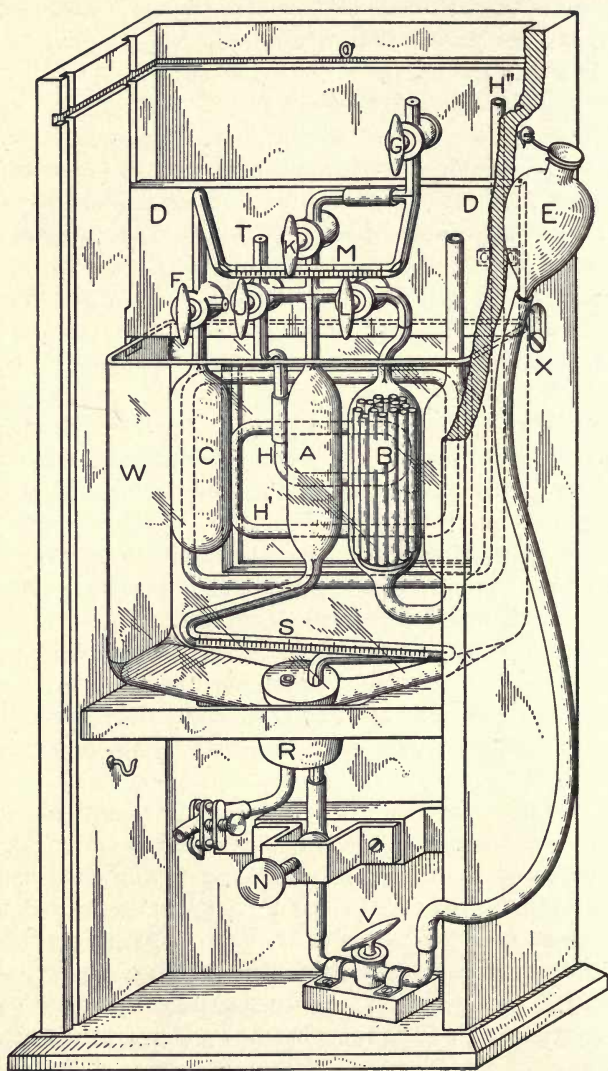


FIG. 107

atmosphere through the side arm whenever necessary. The liquid index in the manometer is introduced through the stopcock *G*.

The burette, pipette, compensating tube, and the copper coil are immersed in water that is contained in a glass cell of rectangular cross section, and that is provided at the lower side with a neck like the neck of a bottle into which the rubber stopper shown in the figure is tightly inserted. In addition to the capillary tube *S* there passes through this rubber stopper a short piece of glass tubing through which the water in the cell may be run off. The glass parts of the apparatus in the cell are fastened to a sliding board *DD* above the cell. If the rubber stopper passing through the neck of the cell is loosened, and the rubber tube is slipped off from the lower end of *S*, the apparatus may be lifted from the case by raising the board to which it is attached. Ready access to all parts of the apparatus is thus easily attained, and the cleaning and repairing of the different portions is rendered easy. Furthermore, the position of the board may be adjusted, within certain limits, by means of the screw *X*, a detail that is of importance in mounting new glass parts of slightly different dimensions from those of the older parts. The case, Fig. 108, is provided with a removable front and top and with a pane of glass at the back to illuminate the apparatus when it stands between the operator and the window.

This form of the Pettersson-Palmqvist apparatus devised by Anderson is only 42 cm. high whereas the original apparatus has a height of 90 cm. Its small size and the ease with which it may be manipulated renders it distinctly superior to the original form.

Before the apparatus is put into use the glass parts should, if necessary, be thoroughly cleaned, and the stopcocks should be carefully lubricated. In preparing the apparatus for use about 30 cc. of distilled mercury is poured into the level-bulb *E* and a small quantity of water is introduced into the burette through

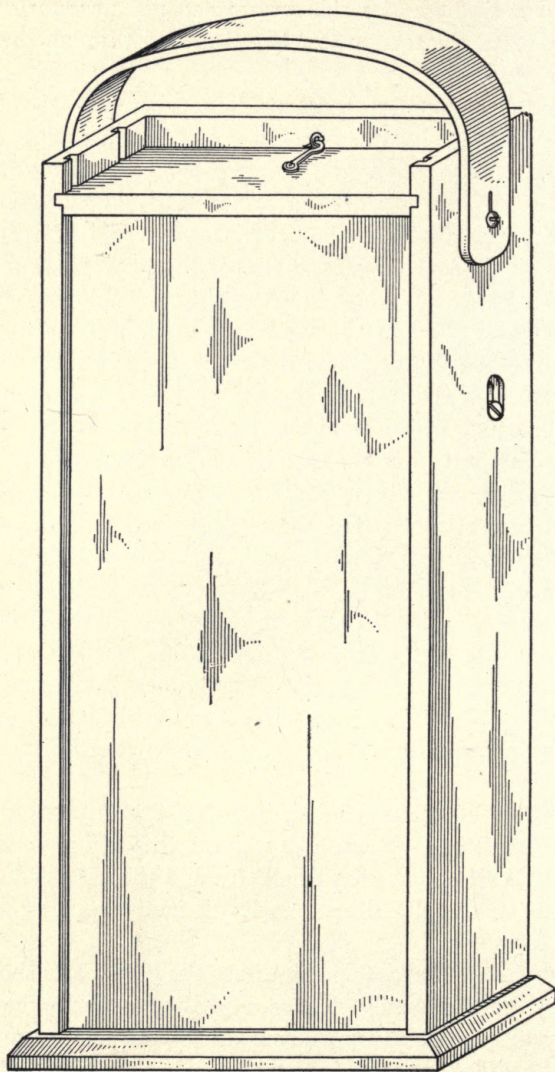


FIG. 108

the opening *T* directly above the stopcock *J*. This is done by covering the end of this capillary tube with a film of water and drawing an amount of the liquid sufficient to form a column from 3 to 5 mm. long in the capillary tube into the burette by lowering the level-bulb.

The drop of liquid that is used in the manometer (petroleum in which azobenzene has been dissolved) is introduced into *M* by filling the burette *A* nearly to the top with mercury with the stopcocks *K* and *G* open, and then closing stopcock *V* and screwing down the compression screw *N*. A small amount of the manometer liquid is now brought upon the end of the capillary tube upon stopcock *G*, and an amount of the liquid sufficient to occupy a length of from 3 to 5 mm. in *M* is drawn into the capillary as far as the branch tube below stopcock *G* by turning back the compression screw *N*. Stopcock *G* is then closed, *F* is opened and the compression screw *N* is again turned down upon the rubber tube, and the liquid is, in this manner, forced into the manometer tube *M*.

The pipette *B* is filled with a solution of potassium hydroxide that is prepared by dissolving one part of potassium hydroxide in two parts of water. This solution is drawn up to the mark on the capillary by lowering the level-bulb *E*, and stopcock *L* is then closed.

Before proceeding with the determination of the carbon dioxide in the air of a room, the apparatus should be allowed to stand long enough in the room to insure equilibrium between the temperature of the water in the water jacket and the temperature of the air in the room. The air in the manometer tube *M* and in the compensating tube *C* should be brought to atmospheric pressure by opening the stopcocks *F* and *G*. During a determination the apparatus should not stand in direct sunlight or in a draft of air.

The actual determination of carbon dioxide is carried on as follows:—Turn stopcock *J* to such position that the burette *A* communicates with the outer air through the tube *T*.

Fill the burette *A* with mercury by opening stopcock *V* and raising the level-bulb *E*. Turn stopcock *J* to such position that the burette *A* communicates with the copper tube *H*, and draw air into *A* through *H* by lowering the level-bulb *E*. Inasmuch as this sample is mixed with air that was already present in the connecting tubes and the copper tube *H*, it is driven out through *T* by turning the stopcock *J* into the proper position and raising the level-bulb. Stopcock *J* is then turned back so that *A* communicates with *H*. The level-bulb *E* is again lowered and the sample of air is drawn into the burette *A* until the mercury in the burette falls slightly below the zero mark on the capillary tube *S*. Stopcock *V* is then closed and the compression screw *N* is turned until the mercury stands exactly at the zero mark. Allow stopcock *J* to remain open for a few moments to allow the air in the burette to assume atmospheric pressure and then close *J*. Open stopcock *K* carefully, and read the position of the liquid in the manometer *M*. Then close stopcock *K*.

To remove the carbon dioxide in the sample, open stopcock *V* and then stopcock *L* and drive the gas over into the pipette *B*. When the mercury nearly reaches the stopcock *L*, close that stopcock and leave the gas in contact with the potassium hydroxide for one minute. Then lower the level-bulb, open stopcock *L*, draw the gas back into the burette, and when the solution of potassium hydroxide rises to the mark on the capillary close stopcock *L*. Bring the mercury approximately to the zero mark in the capillary *S* by raising or lowering level-bulb *E*, close the stopcock *V* and then turn the compression screw *N* until the mercury in the capillary tube *S* stands at such a point above the zero mark as will correspond approximately to the percentage of carbon dioxide in the air under examination. Then open stopcock *K* and turn *N* until the liquid in the manometer stands at the position that is occupied before the absorption was made. The reading of the mercury in the capillary tube *S* now gives directly the amount of carbon dioxide in the sample of air expressed in parts per 10,000.

CHAPTER XIX

THE ANALYSIS OF SALTPETER AND NITRIC ACID ESTERS (NITROGLYCERINE, GUN-COTTON) WITH THE NITROMETER

Walter Crum¹ observed that the higher oxides of nitrogen are completely reduced to nitric oxide when absorbed in sulphuric acid and then shaken with mercury. John Watts² and Georg Lunge³ developed this method still further, and the latter constructed an apparatus therefor which he termed a nitrometer. Hempel utilized⁴ the reaction in the decomposition of the nitric acid esters, and in particular in the determination of the nitroglycerine in dynamite. For this work he designed a special nitrometer which is also admirably adapted to the evaluation of saltpeter. In its original form, however, the Hempel nitrometer is open to objection because the rubber stopper that carries the sample tube is kept in place only with difficulty, and because further of the awkwardness of cleaning the apparatus after a determination has been made. The author has sought to remedy these defects by giving to the nitrometer the form shown in Fig. 109.

The Nitrometer. — The evolution cylinder *C* is provided at the lower end with the double-bore stopcock *T* and the side arm *R*. The stopcock *S*, also of double bore, is attached to the upper end of the cylinder by the carefully ground joint *J* and is held in place by rubber bands slipped over the small glass hooks above and below the joint. *K* is a capillary tube which serves to connect the nitrometer with the gas burette in which

¹ *Philosoph. Mag.* 30 (1847), 426.

² *Chemical News*, 37 (1878), 45.

³ *Berichte der deutschen chemischen Gesellschaft*, 11 (1878), 434.

⁴ *Zeitschrift für analyt. Chemie*, 20 (1881), 82.

the evolved nitric oxide is measured. *L* is a level-bulb that is joined to one arm of the stopcock *T* by a piece of enamelled rubber tubing.

The manipulation of the apparatus in the evaluation of saltpeter or other nitrate is as follows:— Place the evolution

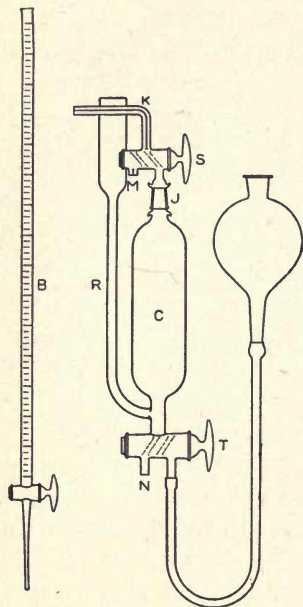


FIG. 109

cylinder *C* in a large clamp and attach it to an iron stand in an upright position. Place the level-bulb *L* in a split ring that is also attached to the rod of the iron stand and introduce into *L* an amount of mercury sufficient to fill the evolution cylinder *C*, the side arm *R*, and the rubber tube joining *L* and *C*. Remove the stopcock *S* from the top of the cylinder *C*, turn the stopcock *T* into such position that *L* and *C* will be in communication, and fill the evolution cylinder *C* with mercury to a point about 5 cm. below the top of the tube *J*. Introduce into the upper end of *C* through the open tube *J* about 5 cc. of a solution of the nitrate to be analyzed, running in the solution from

the small burette *B*, which is calibrated in tenths of a cubic centimeter and can easily be read to fiftieths. Place the stopcock *S* upon *J* and fasten it in position by rubber bands attached to the small hooks on either side of the joint. Raise the level-bulb until the top of the solution in *C* just reaches the lower side of the stopcock *S* and then close *S* and *T*. Lower the level-bulb *L* and then carefully open the stopcock *T* until the mercury in the side arm *R* falls to about the beginning of the bend in that tube.

Introduce a measured amount (about 20 cc.) of concentrated sulphuric acid into the upper open end of *R*. Remove *C* from the clamp and hold it in an inclined position, with the tube *R* on the upper side, at such height that the mercury in *R* stands at the same level as that in the level-bulb *L*. Turn the stopcock *T* to such position that *L* communicates with *C* and then slowly raise *C* (still holding it in an inclined position) until all but about 5 cc. of the sulphuric acid has been drawn into the evolution cylinder *C*. Now lower *C* until the mercury rises to about the middle of the tube *R* and then close the stopcock *T*. Shake the cylinder *C* to insure intimate mixing of the sulphuric acid with the solution of the nitrate. As the reaction proceeds the evolution of gas tends to force the mercury upwards in the side arm *R*. The level of the mercury in this arm is kept approximately the same during the reaction by opening the stopcock *T* from time to time and allowing the mercury to flow back into the level-bulb *L*. The shaking of the evolution cylinder *C* is continued until, with the stopcock *T* closed, no further rise of the mercury in *R* is observed. The reaction is then complete.

C is now again clamped in a vertical position and the capillary tube *K* is attached by means of a small L-shaped piece of capillary tubing to a Hempel gas burette that contains mercury as the confining liquid and into which a very little water has been introduced. The stopcock *S* is then turned to such position as to connect *K* with the outlet *M*, and the level-tube of the burette is raised until the capillary tube *K* is completely filled with mercury. *S* is now turned through 180° so that the cylinder *C* communicates with the tube *K*. *T* is then turned to such position that *L* and *C* are connected, and the evolved gas is drawn over into the burette, the sulphuric acid in the nitrometer being allowed to follow the gas until it almost reaches the end of the capillary tube *K*. The stopcock *S* is then closed, the pinchcock at the top of the burette is also closed and the nitric oxide in the burette is measured in the usual manner, due allowance being made for the tension of water vapor.

After a determination has been made, the nitrometer is cleaned by lowering the level-bulb, opening the stopcocks *S* and *T* and allowing the *clean* mercury to flow back into the bulb *L*. The stopcock *T* is then turned into the position shown in the figure and the dirty mercury, mercurous sulphate, and sulphuric acid are allowed to run out through the tube *N* into a beaker. The stopcock *S* is next slipped off from the upper end of the cylinder *C* and the side arm *R* as well as the wide tube of the stopcock *S* are thoroughly rinsed with water and are then dried.

In calculating the results of the analysis allowance must be made for the solubility of nitric oxide in sulphuric acid. 15 cc. of sulphuric acid will dissolve about 0.2 cc. of nitric oxide.

The purity of the nitric oxide that is evolved may be ascertained by passing the gas, after it has been measured in the burette, into a double gas pipette for liquid reagents that contains in the first two bulbs a solution of a ferrous salt, and in the last two, water. The analytical absorbing power of a saturated solution of ferrous chloride is 14, and of ferrous sulphate about 4.

In the evaluation of saltpeter the sample should be dissolved in a little water and 5 cc. of this solution is used in the analysis. The concentration of this solution should be such that about 75 cc. of nitric oxide will be evolved.

In the analysis of solid material a weighed sample of the substance is introduced into the upper open end of the evolution cylinder *C*. The sample is moistened with a little water, the stopcock *S* is then placed in position and fastened with rubber bands, mercury is driven up to the lower side of the stopcock *S*, and the further analysis is then carried out in the manner above described.

In the analysis of gun-cotton Hagen first shakes the sample with concentrated sulphuric acid in the evolution cylinder *C* for three minutes, and then when the gun-cotton is dissolved, he heats *C* by holding it in an inclined position over a Bunsen burner, and continues the shaking of *C* as long as evolution of gas is observed.

CHAPTER XX

THE LUNGE NITROMETER

The nitrometer of Lunge¹ was originally designed for the evaluation of nitrates. For this specific purpose it is inferior to the nitrometer described in Chapter XIX, because the nitric oxide is evolved in the tube in which the gas volume is finally read, and the foaming of the acid renders difficult the accurate reading of the height of the confining liquid.

A modified form of his nitrometer which Lunge later described² under the name of a ureometer, but which is generally known under the name of the Lunge nitrometer, is an instrument of wide application in gas-volumetric analysis.³

The Lunge Nitrometer. — The instrument (Fig. 110) consists of a gas burette *A*, a level-tube *B*, and an evolution flask *C*. The burette has a capacity of more than 100 cc. It is provided at the upper end with a two-bore stopcock, and is graduated from the stopcock downward in $\frac{1}{8}$ cc.

One of the two tubes of the stopcock is a short upright capillary tube of the usual diameter: the other tube is somewhat larger and is bent over until it points nearly downward. To it the evolution flask *C* is joined by a short piece of rubber tubing, the ends of the glass tubes being brought nearly together.

The evolution flask *C* usually has a capacity of about 100 cc. A short tube, open at the top, is fused to the bottom of the flask. A soft, one-hole rubber stopper carrying a short glass tube is inserted in the neck of *C*.

¹ *Berichte der deutschen chemischen Gesellschaft*, 11 (1878), 434; *ibid.*, 21 (1888), 376.

² *Berichte der deutschen chemischen Gesellschaft*, 18 (1885), 2030.

³ See A. H. Allen, *J. Soc. Chem. Ind.* 4 (1885), 178; Lunge, *Chemische Industrie*, 1885, 161; *J. Soc. Chem. Ind.*, 9 (1890), 21.

Manipulation of the Lunge Nitrometer. — In making a determination with the nitrometer, water or mercury is poured into the open end of the level-tube *B*, the stopcock *D* is

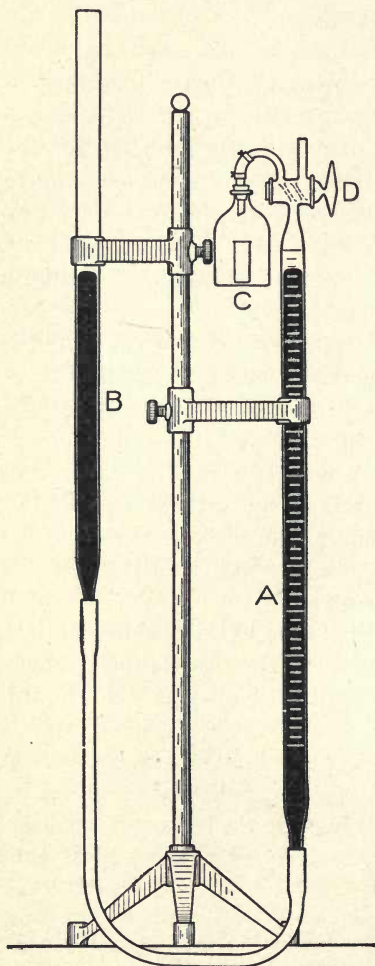


FIG. 110

opened, and the confining liquid is allowed to rise nearly to the stopcock which is then closed. The reacting substances are now placed in the evolution flask *C*, one in the outer space, the other in the tube. The short rubber tube carrying the stopper of *C* is slipped over the end of the bent tube of *D*, and the rubber stopper is then tightly inserted into the neck of the evolution flask. In doing this the neck of the evolution flask should be grasped between the thumb and fingers of one hand and the stopper be pushed into the neck of the flask with the other hand. The body of the flask itself should not be touched by the hand during the operation because this would warm the air in the flask and would cause error in the next adjustment. The air in *C* is slightly compressed by the insertion of the stopper. It is brought to atmospheric pressure by turning the stopcock *D* so that the evolution

flask connects with the burette, and then bringing the confining liquid in the level-tube to the same height as that in the burette. The air in the evolution flask is now at atmospheric pressure. The stopcock *D* is turned through 180° while the tubes are in this position, and the level-tube is then raised until all of the air in the burette is driven out through the open capillary tube of the stopcock. The stopcock is turned to join *A* to *C*, and the substances in the evolution flask *C* are then brought together by taking hold of the rubber stopper of the flask and tipping it. The flask itself should not be touched with the hand. The reaction is allowed to proceed to completion, the flask being occasionally gently shaken. The gas that is set free passes over into the burette. The pressure thus caused is relieved from time to time by lowering the level-tube. When the evolution of gas has ceased, the confining liquid in the burette and level-tube is brought to the same height, and the volume of gas in the burette is read off.¹ The thermometer and barometer are read and the gas volume is corrected to standard conditions. The necessity for this correction may be avoided by using the Lunge gas volumeter (see p. 37) in place of the nitrometer.

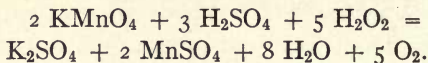
As illustrative of the many and various gas volumetric determinations that may be made with the Lunge nitrometer (or with the Lunge gas volumeter) the standardization of potassium permanganate, the determination of the active oxygen in hydrogen dioxide, the determination of the available chlorine in "chloride of lime," the evaluation of pyrolusite, and the determination of carbon dioxide in sodium carbonate will here be described.

The nitrometer should be thoroughly rinsed with distilled water before a determination is begun, and the evolution flask should be carefully cleaned and dried. The apparatus should

¹ If the heat of reaction of the substances in the evolution flask is appreciable, a beaker containing water of the temperature of the room should be brought up under the flask after the reaction is complete and the flask should be allowed to stand immersed in the water for a period of five minutes before the volume of gas in the burette is measured.

stand in a room of even temperature and should be protected from direct sunlight and drafts of air. The manipulation general to all of the various determinations has already been described above.

The Standardization of Potassium Permanganate. — A solution of potassium permanganate that is acidulated with sulphuric acid reacts upon hydrogen dioxide in accordance with the equation —



From this it appears that

80 parts by weight of oxygen is equivalent to 158.03 parts by weight of KMnO_4 .

Since one cc. of oxygen, under standard conditions, weighs 0.00143 gram, each cubic centimeter of evolved oxygen, reduced to standard conditions, is equivalent to 0.0028247 gram of KMnO_4 .

If the solution of potassium permanganate is approximately decinormal in strength, 25 cc. of the solution is placed in the outer compartment of the evolution flask, and 5 cc. of normal sulphuric acid is added to it. About 5 cc. of a 3% solution of hydrogen dioxide is then placed in the inner tube of the flask.

The apparatus is now connected up, the air in the evolution flask is brought to atmospheric pressure, the stopcock of the burette is turned so that the flask communicates with the burette, and the evolution flask is then tipped and the hydrogen dioxide is slowly run out into the solution of potassium permanganate, the evolution bottle being constantly shaken. The level-tube is lowered from time to time to keep the gas in the burette at approximately atmospheric pressure. After the evolution of the oxygen has ceased, the gas is measured and is reduced to standard conditions. The solution in the evolution flask should be colorless after the reaction has taken place. If

it should still show the color of potassium permanganate, too little hydrogen dioxide has been used. If 25 cc. of the solution of potassium permanganate has been used in the determination, the grams of KMnO_4 per liter of solution is calculated as follows:

$$25 : 100 = \text{cc. O}_2 \times 0.0028247 : \text{grams KMnO}_4 \text{ per liter.}$$

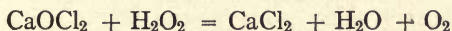
The Determination of Active Oxygen in Hydrogen Dioxide. — The reaction between acidulated potassium permanganate and hydrogen dioxide that has just been discussed is utilized in this determination also.

A saturated solution of potassium permanganate is employed, and an amount of this solution (usually about 10 cc.) more than sufficient to convert all of the sample of hydrogen dioxide into water and oxygen is placed in the inner tube of the evolution flask.

If commercial hydrogen dioxide of the usual strength (about 3 per cent) is under examination, it must first be diluted. 10 cc. of the solution is run into a 100 cc. measuring flask from a pipette or burette, and the flask is then filled to the mark and is shaken. 10 cc. of this diluted solution of hydrogen dioxide and 20 cc. of dilute (normal) sulphuric acid are placed in the outer space of the evolution flask. The reaction is now effected in the usual manner. The solution in the evolution flask must show the color of potassium permanganate after the evolution of oxygen has ceased. If the liquid is colorless, it indicates that too little potassium permanganate has been used, and that the hydrogen dioxide has not been completely decomposed.

The results are calculated in the manner described under the preceding determination, due allowance being made for the dilution of the hydrogen dioxide.

The Determination of the Available Chlorine in "Chloride of Lime." — *Chloride of lime* acts upon hydrogen dioxide as follows:



Each molecule of oxygen evolved is equivalent to a molecule of available chlorine in the bleaching powder, or

$$1 \text{ cc. O}_2 = 1 \text{ cc. Cl}_2 = 0.003166 \text{ gram chlorine.}$$

The calculation of the result of the analysis is simplified if a sample of bleaching powder of exactly 0.3166 gram is used, for then

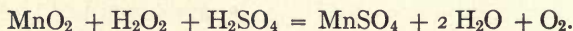
$$1 \text{ cc. oxygen} = 1 \text{ per cent available chlorine.}$$

7.917 grams of the sample of *chloride of lime* is placed in a 250 cc. measuring flask which is then filled up to the mark and thoroughly shaken. 10 cc. of the resulting turbid bleach solution, which will contain 0.3166 gram of the chloride of lime, is drawn up into a pipette and is run into the outer compartment of the evolution flask. The measuring flask should be vigorously shaken just before the sample is drawn off into the pipette.

About six cc. of a solution of hydrogen dioxide containing approximately 1.5 per cent H_2O_2 is introduced into the inner tube of the flask, and the determination is then carried out in the usual manner.

The evolved oxygen is reduced to standard conditions. Each cubic centimeter of the gas is equivalent to one per cent of available chlorine in the *chloride of lime*.

The Evaluation of Pyrolusite. — Manganese dioxide reacts with hydrogen dioxide in the presence of sulphuric acid in accordance with the equation —



$$1 \text{ cc. evolved oxygen} = 0.003885 \text{ gram MnO}_2.$$

If 0.3885 gram of pyrolusite is used in the determination, each cubic centimeter of evolved oxygen, reduced to standard conditions, is equivalent to one per cent of MnO_2 in the ore.

The weighed sample of very finely powdered manganese ore is placed in the outer compartment of the evolution flask. 5 cc. of a normal solution of sulphuric acid is run in upon the pyrolusite. 25 cc. of a three per cent solution of hydrogen dioxide is next introduced into the inner tube of the flask. The flask is allowed to stand unstoppered for about five minutes or until the sulphuric acid has decomposed any carbonates that may be present in the pyrolusite. When the evolution of gas from the material in the outer compartment of the evolution flask has entirely ceased, the flask is connected to the gas burette in the usual manner and the hydrogen dioxide is brought into contact with the pyrolusite. The evolution flask is shaken for two minutes at the end of which time the reaction should be complete. If black particles of pyrolusite are still to be seen in the flask, the determination should be discarded and the ore should be more finely ground before a fresh sample is weighed out. The evolution flask should be shaken from time to time. If 0.3885 gram of pyrolusite has been used, the number of cubic centimeters of evolved oxygen, reduced to standard conditions, represents the per cent of manganese dioxide in the ore.

The Determination of Carbon Dioxide in Sodium Carbonate. — In this determination the nitrometer should be filled with mercury instead of with water as the confining liquid because of the solubility of carbon dioxide in water.

About 0.15 gram of the dry sodium carbonate or sodium bicarbonate under examination is accurately weighed and is placed in the outer compartment of the evolution flask. 5 cc. of a normal solution of sulphuric acid is placed in the inner compartment, the flask is connected with the burette and is then carefully tilted so that the sulphuric acid *slowly* drops upon the sodium carbonate. When all of the acid has been poured upon the salt the evolution flask should be thoroughly shaken. The carbon dioxide evolved is measured and is reduced to standard conditions. Since one cubic centimeter of carbon dioxide weighs 0.001965 gram, the weight of the evolved carbon dioxide is equal

to the corrected volume of the gas in cubic centimeters multiplied by 0.001965.

$$\text{Per cent CO}_2 = \frac{100 \times \text{grams CO}_2 \text{ evolved}}{\text{weight sodium carbonate in grams.}}$$

Some carbon dioxide will of course remain dissolved in the liquid in the evolution flask. If very accurate results are desired it is preferable to employ a different method for this determination rather than to attempt to introduce a correction for the amount of this dissolved gas.

International Atomic Weights, 1913

		SYMBOL	ATOMIC WEIGHT			SYMBOL	ATOMIC WEIGHT
Aluminum	Al	27.1	Neodymium	Nd	144.3		
Antimony	Sb	120.2	Neon	Ne	20.2		
Argon	A	39.88	Nickel	Ni	58.68		
Arsenic	As	74.96	Niton (radium emanation)	Nt	222.4		
Barium	Ba	137.37	Nitrogen	N	14.01		
Bismuth	Bi	208.0	Osmium	Os	190.9		
Boron	B	11.0	Oxygen	O	16.00		
Bromine	Br	79.92	Palladium	Pd	106.7		
Cadmium	Cd	112.40	Phosphorus	P	31.04		
Caesium	Cs	132.81	Platinum	Pt	195.2		
Calcium	Ca	40.07	Potassium	K	39.10		
Carbon	C	12.00	Praseodymium	Pr	140.6		
Cerium	Ce	140.25	Radium	Ra	226.4		
Chlorine	Cl	35.46	Rhodium	Rh	102.9		
Chromium	Cr	52.0	Rubidium	Rb	85.45		
Cobalt	Co	58.97	Ruthenium	Ru	101.7		
Columbium	Cb	93.5	Samarium	Sa	150.4		
Copper	Cu	63.57	Scandium	Sc	44.1		
Dysprosium	Dy	162.5	Selenium	Se	79.2		
Erbium	Er	167.7	Silicon	Si	28.3		
Europium	Eu	152.0	Silver	Ag	107.88		
Fluorine	F	19.0	Sodium	Na	23.00		
Gadolinium	Gd	157.3	Strontium	Sr	87.63		
Gallium	Ga	69.9	Sulphur	S	32.07		
Germanium	Ge	72.5	Tantalum	Ta	181.5		
Glucinum	Gl	9.1	Tellurium	Te	127.5		
Gold	Au	197.2	Terbium	Tb	159.2		
Helium	He	3.99	Thallium	Tl	204.0		
Holmium	Ho	163.5	Thorium	Th	232.4		
Hydrogen	H	1.008	Thulium	Tm	168.5		
Indium	In	114.8	Tin	Sn	119.0		
Iodine	I	126.92	Titanium	Ti	48.1		
Iridium	Ir	193.1	Tungsten	W	184.0		
Iron	Fe	55.84	Uranium	U	238.5		
Krypton	Kr	82.92	Vanadium	V	51.0		
Lanthanum	La	139.0	Xenon	Xe	130.2		
Lead	Pb	207.10	Ytterbium (Neoytterbium)	Yb	172.0		
Lithium	Li	6.94	Yttrium	Yt	89.0		
Lutecium	Lu	174.0	Zinc	Zn	65.37		
Magnesium	Mg	24.32	Zirconium	Zr	90.6		
Manganese	Mn	54.93					
Mercury	Hg	200.6					
Molybdenum	Mo	96.0					

Theoretical Densities of Gases

and Weights of One Liter of the Same at 0° and 760 mm. pressure, at Sea Level and Latitude 45°

Substance	Formula	Molecular Weight	Density Air = 1	Weight of One Liter in Grams
Acetylene	C_2H_2	26.02	0.8988	1.1620
Allylene	C_3H_4	40.03	1.3819	1.7869
Ammonia	NH_3	17.03	0.5895	0.7621
Arsine	AsH_3	77.98	2.696	3.485
Bromine	Br_2	159.84	5.5249	7.1426
Butane	C_4H_{10}	58.08	2.0065	2.594
Butylene	C_4H_8	56.06	1.9349	2.5019
Carbon dioxide	CO_2	44.00	1.5201	1.9652
Carbon monoxide	CO	28.00	0.9673	1.2506
Carbon oxysulphide	COS	60.07	2.0749	2.6825
Carbonyl chloride	$COCl_2$	98.92	3.4168	4.4172
Chlorine	Cl_2	70.92	2.4494	3.1666
Cyanogen	C_2N_2	52.02	1.7993	2.3261
Ethane	C_2H_6	30.05	1.0381	1.3421
Ethylene	C_2H_4	28.03	0.9684	1.2520
Hydrogen	H_2	2.016	0.06965	0.09004
Hydrogen bromide	HBr	80.93	2.7973	3.6163
Hydrogen chloride	HCl	36.47	1.2595	1.6283
Hydrogen fluoride	HF	20.	0.691	0.894
Hydrogen iodide	HI	127.93	4.4172	5.7106
Hydrogen selenide	H_2Se	81.2	2.806	3.627
Hydrogen sulphide	H_2S	34.09	1.1773	1.5230
Hydrogen telluride	H_2Te	129.5	4.478	5.789
Methane	CH_4	16.03	0.5539	0.7160
Nitric oxide	NO	30.01	1.0378	1.3417
Nitrogen	N_2	28.02	0.9701	1.2542
Nitrogen tetroxide	NO_2	46.01	1.5906	2.0563
Nitrous oxide	N_2O	44.02	1.5229	1.9688
Oxygen	O_2	32.00	1.1055	1.4292
Phosphine	PH_3	34.06	1.175	1.520
Propane	C_3H_8	44.06	1.5204	1.966
Propylene	C_3H_6	42.05	1.4527	1.8780
Silicon tetrafluoride	SiF_4	104.3	3.607	4.663
Sulphur dioxide	SO_2	64.07	2.2131	2.8611
Water vapor	H_2O	18.016	0.6218	0.8040
Atmospheric air			1.0000	1.2928

Reduction of a Gas Volume to 0° and 760 mm.

If v is the volume of a gas at t° and p mm. pressure, the volume v_0 of the gas at 0° and 760 mm. may be calculated with the aid of the formula

$$v_0 = v \frac{p}{760 (1 + 0.00367 t)}.$$

To facilitate the reduction of gas volumes to standard conditions, the values of the expression $(1 + 0.00367t)$ from -2° to $+34^\circ$ are given in the following table:

t	$1 + 0.00367 t$	$\text{Log} \frac{1}{1 + 0.00367 t}$	t	$1 + 0.00367 t$	$\text{Log} \frac{1}{1 + 0.00367 t}$
$-2^\circ.0$	0, 99266	0, 00320	$1^\circ.1$	1, 00404	9, 99825
-1.9	99303	00304	1.2	00440	99809
-1.8	99339	00288	1.3	00477	99793
-1.7	99376	00272	1.4	00514	99777
-1.6	99413	00256	1.5	00551	99761
-1.5	99449	00240	1.6	00587	99746
-1.4	99486	00224	1.7	00624	99730
-1.3	99523	00208	1.8	00661	99714
-1.2	99560	00192	1.9	00697	99698
-1.1	99596	00176	2.0	00734	99682
-1.0	99633	00160		1, 00771	9, 99666
	0, 99670	0, 00144	2.1	00807	99651
-0.9	99706	00128	2.2	00844	99635
-0.8	99743	00112	2.3	00881	99619
-0.7	99780	00096	2.4	00918	99603
-0.6	99816	00080	2.5	00954	99588
-0.5	99853	00064	2.6	00991	99572
-0.4	99890	00048	2.7	01028	99556
-0.3	99927	00032	2.8	01064	99540
-0.2	99963	00016	2.9	01101	99524
-0.1	99996	00000	3.0	01138	9, 99509
0.0	100000	00000		1, 01174	9, 99493
	1, 00037	9, 99984	3.1	01211	99477
$+0.1$	00073	99968	3.2	01248	99461
0.2	00110	99952	3.3	01285	99445
0.3	00147	99936	3.4	01321	99430
0.4	00184	99920	3.5	01358	99414
0.5	00220	99905	3.6	01395	99398
0.6	00257	99889	3.7	01431	99383
0.7	00294	99873	3.8	01468	99367
0.8	00330	99857			
0.9	00367	99841			
1.0					

Reduction of a Gas Volume to 0° and 760 mm.

Value of $(1 + 0.00367 t)$ for $t = 4.1$ to 14.0°

t	$1 + 0.00367 t$	$\text{Log} \frac{1}{1 + 0.00367 t}$	t	$1 + 0.00367 t$	$\text{Log} \frac{1}{1 + 0.00367 t}$
	I,	9, —10		I,	9, —10
4°.1	01505	99351	9°.1	03340	98573
4.2	01541	99336	9.2	03376	98558
4.3	01578	99320	9.3	03413	98542
4.4	01615	99304	9.4	03450	98527
4.5	01652	99288	9.5	03487	98511
4.6	01688	99273	9.6	03523	98496
4.7	01725	99257	9.7	03560	98481
4.8	01762	99241	9.8	03597	98465
4.9	01798	99226	9.9	03633	98450
5.0	01835	99210	10.0	03670	98435
	I,	9, —10		I,	9, —10
5.1	01872	99195	10.1	03707	98420
5.2	01908	99179	10.2	03743	98404
5.3	01945	99163	10.3	03780	98389
5.4	01982	99148	10.4	03817	98373
5.5	02019	99132	10.5	03854	98358
5.6	02055	99117	10.6	03890	98343
5.7	02092	99101	10.7	03927	98327
5.8	02129	99085	10.8	03964	98312
5.9	02165	99070	10.9	04000	98297
6.0	02202	99054	11.0	04037	98281
	I,	9, —10		I,	9, —10
6.1	02239	99038	11.1	04074	98266
6.2	02275	99023	11.2	04110	98251
6.3	02312	99007	11.3	04147	98235
6.4	02349	98992	11.4	04184	98220
6.5	02386	98976	11.5	04221	98204
6.6	02422	98961	11.6	04257	98189
6.7	02459	98945	11.7	04294	98174
6.8	02496	98929	11.8	04331	98159
6.9	02532	98914	11.9	04367	98144
7.0	02569	98899	12.0	04404	98128
	I,	9, —10		I,	9, —10
7.1	02606	98883	12.1	04441	98113
7.2	02642	98867	12.2	04477	98098
7.3	02679	98852	12.3	04514	98083
7.4	02716	98836	12.4	04551	98067
7.5	02753	98821	12.5	04588	98052
7.6	02789	98805	12.6	04624	98037
7.7	02826	98790	12.7	04661	98022
7.8	02863	98774	12.8	04698	98006
7.9	02899	98759	12.9	04734	97991
8.0	02936	98743	13.0	04771	97976
	I,	9, —10		I,	9, —10
8.1	02973	98728	13.1	04808	97961
8.2	03009	98712	13.2	04844	97945
8.3	03046	98697	13.3	04881	97930
8.4	03083	98681	13.4	04918	97915
8.5	03120	98666	13.5	04955	97900
8.6	03156	98651	13.6	04991	97885
8.7	03193	98635	13.7	05028	97869
8.8	03230	98619	13.8	05065	97854
8.9	03266	98604	13.9	05101	97839
9.0	03303	98589	14.0	05138	97824

Reduction of a Gas Volume to 0° and 760 mm.

Value of $(1 + 0.00367 t)$ for $t = 14.1$ to 24.0°

t	$1 + 0.00367 t$	$\text{Log} \frac{1}{1 + 0.00367 t}$	t	$1 + 0.00367 t$	$\text{Log} \frac{1}{1 + 0.00367 t}$
	I,	9, —10		I,	9, —10
14°.1	05175	97809	19°.1	07010	97058
14.2	05211	97794	19.2	07046	97043
14.3	05248	97779	19.3	07083	97028
14.4	05285	97763	19.4	07120	97013
14.5	05322	97748	19.5	07157	96998
14.6	05358	97733	19.6	07193	96983
14.7	05395	97718	19.7	07230	96968
14.8	05432	97703	19.8	07267	96954
14.9	05468	97688	19.9	07303	96939
15.0	05505	97673	20.0	07340	96924
	I,	9, —10		I,	9, —10
15.1	05542	97657	20.1	07377	96909
15.2	05578	97642	20.2	07413	96894
15.3	05615	97627	20.3	07450	96879
15.4	05652	97612	20.4	07487	96864
15.5	05689	97597	20.5	07524	96850
15.6	05725	97582	20.6	07560	96835
15.7	05762	97567	20.7	07597	96820
15.8	05799	97552	20.8	07634	96805
15.9	05835	97537	20.9	07670	96791
16.0	05872	97522	21.0	07707	96776
	I,	9, —10		I,	9, —10
16.1	05909	97507	21.1	07744	96761
16.2	05945	97492	21.2	07780	96746
16.3	05982	97477	21.3	07817	96731
16.4	06019	97462	21.4	07854	96716
16.5	06056	97447	21.5	07891	96702
16.6	06092	97432	21.6	07927	96687
16.7	06129	97417	21.7	07964	96672
16.8	06166	97402	21.8	08001	96657
16.9	06202	97387	21.9	08037	96643
17.0	06239	97372	22.0	08074	96628
	I,	9, —10		I,	9, —10
17.1	06276	97357	22.1	08111	96613
17.2	06312	97342	22.2	08147	96598
17.3	06349	97327	22.3	08184	96584
17.4	06386	97312	22.4	08221	96569
17.5	06423	97297	22.5	08258	96554
17.6	06459	97282	22.6	08294	96539
17.7	06496	97267	22.7	08331	96525
17.8	06533	97252	22.8	08368	96510
17.9	06569	97237	22.9	08404	96495
18.0	06606	97222	23.0	08441	96481
	I,	9, —10		I,	9, —10
18.1	06643	97207	23.1	08478	96466
18.2	06679	97192	23.2	08514	96451
18.3	06716	97177	23.3	08551	96437
18.4	06753	97162	23.4	08588	96422
18.5	06790	97147	23.5	08625	96407
18.6	06826	97132	23.6	08661	96393
18.7	06863	97117	23.7	08698	96378
18.8	06900	97102	23.8	08735	96363
18.9	06936	97088	23.9	08771	96349
19.0	06973	97073	24.0	08808	96334

Reduction of a Gas Volume to 0° and 760 mm.

Value of $(1 + 0.00367 t)$ for $t = 24.1$ to 34.0° .

t	$1 + 0.00367 t$	$\text{Log} \frac{1}{1 + 0.00367 t}$	t	$1 + 0.00367 t$	$\text{Log} \frac{1}{1 + 0.00367 t}$
	I,	9, —10		I,	9, —10
24°.1	08845	96319	29°.1	10680	95593
24.2	08881	96305	29.2	10716	95579
24.3	08918	96290	29.3	10753	95565
24.4	08955	96275	29.4	10790	95550
24.5	08992	96261	29.5	10827	95535
24.6	09028	96246	29.6	10863	95521
24.7	09065	96231	29.7	10900	95507
24.8	09102	96217	29.8	10937	95492
24.9	09138	96202	29.9	10973	95478
25.0	09175	96188	30.0	11010	95464
	I,	9, —10		I,	9, —10
25.1	09212	96173	30.1	11047	95449
25.2	09248	96159	30.2	11083	95435
25.3	09285	96144	30.3	11120	95421
25.4	09322	96129	30.4	11157	95406
25.5	09359	96115	30.5	11194	95392
25.6	09395	96100	30.6	11230	95378
25.7	09432	96086	30.7	11267	95363
25.8	09469	96071	30.8	11304	95349
25.9	09505	96057	30.9	11340	95335
26.0	09542	96042	31.0	11377	95320
	I,	9, —10		I,	9, —10
26.1	09579	96027	31.1	11414	95306
26.2	09615	96013	31.2	11450	95292
26.3	09652	95998	31.3	11487	95278
26.4	09689	95984	31.4	11524	95263
26.5	09726	95969	31.5	11561	95249
26.6	09762	95955	31.6	11597	95235
26.7	09799	95940	31.7	11634	95220
26.8	09836	95925	31.8	11671	95206
26.9	09872	95901	31.9	11707	95192
27.0	09909	95897	32.0	11744	95178
	I,	9, —10		I,	9, —10
27.1	09946	95882	32.1	11781	95163
27.2	09982	95868	32.2	11817	95149
27.3	10019	95853	32.3	11854	95135
27.4	10056	95839	32.4	11891	95120
27.5	10093	95824	32.5	11928	95106
27.6	10129	95810	32.6	11964	95092
27.7	10166	95795	32.7	12001	95078
27.8	10203	95781	32.8	12038	95064
27.9	10239	95767	32.9	12074	95049
28.0	10276	95752	33.0	12111	95035
	I,	9, —10		I,	9, —10
28.1	10313	95737	33.1	12148	95021
28.2	10349	95723	33.2	12184	95007
28.3	10386	95709	33.3	12221	94993
28.4	10423	95694	33.4	12258	94978
28.5	10460	95679	33.5	12295	94964
28.6	10496	95665	33.6	12331	94950
28.7	10533	95651	33.7	12368	94936
28.8	10570	95636	33.8	12405	94922
28.9	10606	95622	33.9	12441	94907
29.0	10643	95608	34.0	12478	94893

Tension of Aqueous Vapor

Expressed in millimeters of mercury at 0°, density of mercury

= 13.59593 at latitude 45° and at the sea-level

Calculated from Regnault's measurements by Broch (Trav. et

Mém. du Bur. intern. des Poids et Mes. I A. 33, 1881)

<i>t</i>	Tension	<i>t</i>	Tension	<i>t</i>	Tension	<i>t</i>	Tension
	mm.		mm.		mm.		mm.
—2°.0	3.9499	2°.6	5.5008	7°.1	7.5171	11°.6	10.1614
—1.9	3.9790	2.7	5.5398	7.2	7.5685	11.7	10.2285
—1.8	4.0082	2.8	5.5790	7.3	7.6202	11.8	10.2960
—1.7	4.0376	2.9	5.6185	7.4	7.6722	11.9	10.3639
—1.6	4.0672	3.0	5.6582	7.5	7.7246	12.0	10.4322
—1.5	4.0970			7.6	7.7772		
—1.4	4.1271	3.1	5.6981	7.7	7.8302	12.1	10.5009
—1.3	4.1574	3.2	5.7383	7.8	7.8834	12.2	10.5700
—1.2	4.1878	3.3	5.7788	7.9	7.9370	12.3	10.6394
—1.1	4.2185	3.4	5.8195	8.0	7.9909	12.4	10.7093
		3.5	5.8605			12.5	10.7796
—1.0	4.2493	3.6	5.9017	8.1	8.0452	12.6	10.8503
—0.9	4.2803	3.7	5.9432	8.2	8.0998	12.7	10.9214
—0.8	4.3116	3.8	5.9850	8.3	8.1547	12.8	10.9928
—0.7	4.3430	3.9	6.0270	8.4	8.2099	12.9	11.0647
—0.6	4.3747	4.0	6.0693	8.5	8.2655	13.0	11.1370
—0.5	4.4065			8.6	8.3214		
—0.4	4.4385	4.1	6.1118	8.7	8.3777	13.1	11.2097
—0.3	4.4708	4.2	6.1546	8.8	8.4342	13.2	11.2829
—0.2	4.5032	4.3	6.1977	8.9	8.4911	13.3	11.3564
—0.1	4.5359	4.4	6.2410	9.0	8.5484	13.4	11.4304
		4.5	6.2846			13.5	11.5048
0.0	4.5687	4.6	6.3285			13.6	11.5797
+0.1	4.6017	4.7	6.3727	9.1	8.6061	13.7	11.6550
0.2	4.6350	4.8	6.4171	9.2	8.6641	13.8	11.7307
0.3	4.6685	4.9	6.4618	9.3	8.7224	13.9	11.8069
0.4	4.7022	5.0	6.5067	9.4	8.7810	14.0	11.8835
0.5	4.7361			9.5	8.8400		
0.6	4.7703			9.6	8.8993		
0.7	4.8047	5.1	6.5519	9.7	8.9589	14.1	11.9605
0.8	4.8393	5.2	6.5974	9.8	9.0189	14.2	12.0380
0.9	4.8741	5.3	6.6432	9.9	9.0792	14.3	12.1159
1.0	4.9091	5.4	6.6893	10.0	9.1398	14.4	12.1943
		5.5	6.7357			14.5	12.2731
1.1	4.9443	5.6	6.7824	10.1	9.2009	14.6	12.3523
1.2	4.9798	5.7	6.8293	10.2	9.2623	14.7	12.4320
1.3	5.0155	5.8	6.8765	10.3	9.3241	14.8	12.5122
1.4	5.0515	5.9	6.9240	10.4	9.3863	14.9	12.5928
1.5	5.0877	6.0	6.9718	10.5	9.4488	15.0	12.6739
1.6	5.1240			10.6	9.5117		
1.7	5.1606	6.1	7.0198	10.7	9.5750	15.1	12.7554
1.8	5.1975	6.2	7.0682	10.8	9.6387	15.2	12.8374
1.9	5.2346	6.3	7.1168	10.9	9.7027	15.3	12.9198
2.0	5.2719	6.4	7.1658	11.0	9.7671	15.4	13.0027
		6.5	7.2150			15.5	13.0861
2.1	5.3094	6.6	7.2646	11.1	9.8318	15.6	13.1700
2.2	5.3472	6.7	7.3145	11.2	9.8969	15.7	13.2543
2.3	5.3852	6.8	7.3647	11.3	9.9624	15.8	13.3392
2.4	5.4235	6.9	7.4152	11.4	10.0283	15.9	13.4245
2.5	5.4620	7.0	7.4660	11.5	10.0946	16.0	13.5103

Tension of Aqueous Vapor. — *Continued*

<i>t</i>	Tension	<i>t</i>	Tension	<i>t</i>	Tension	<i>t</i>	Tension
	mm.		mm.		mm.		mm.
16°.1	13.5965	20°.6	18.0176	25°.1	23.6579	29°.6	30.7928
16.2	13.6832	20.7	18.1288	25.2	23.7991	29.7	30.9707
16.3	13.7705	20.8	18.2406	25.3	23.9411	29.8	31.1494
16.4	13.8582	20.9	18.3529	25.4	24.0838	29.9	31.3291
16.5	13.9464	21.0	18.4659	25.5	24.2272	30.0	31.5096
16.6	14.0351			25.6	24.3714		
16.7	14.1243	21.1	18.5795	25.7	24.5164	30.1	31.6910
16.8	14.2141	21.2	18.6937	25.8	24.6620	30.2	31.8734
16.9	14.3043	21.3	18.8085	25.9	24.8084	30.3	32.0567
17.0	14.3950	21.4	18.9240	26.0	24.9556	30.4	32.2410
		21.5	19.0400			30.5	32.4262
17.1	14.4862	21.6	19.1567	26.1	25.1035	30.6	32.6124
17.2	14.5779	21.7	19.2740	26.2	25.2523	30.7	32.7995
17.3	14.6702	21.8	19.3920	26.3	25.4018	30.8	32.9875
17.4	14.7630	21.9	19.5105	26.4	25.5521	30.9	33.1765
17.5	14.8563	22.0	19.6297	26.5	25.7032	31.0	33.3664
17.6	14.9501			26.6	25.8551		
17.7	15.0444	22.1	19.7496	26.7	26.0077	31.1	33.5573
17.8	15.1392	22.2	19.8701	26.8	26.1612	31.2	33.7491
17.9	15.2345	22.3	19.9912	26.9	26.3155	31.3	33.9419
18.0	15.3304	22.4	20.1130	27.0	26.4705	31.4	34.1356
		22.5	20.2355			31.5	34.3303
18.1	15.4268	22.6	20.3586	27.1	26.6263	31.6	34.5259
18.2	15.5237	22.7	20.4824	27.2	26.7830	31.7	34.7225
18.3	15.6212	22.8	20.6068	27.3	26.9405	31.8	34.9201
18.4	15.7192	22.9	20.7319	27.4	27.0987	31.9	35.1186
18.5	15.8178	23.0	20.8576	27.5	27.2578	32.0	35.3181
18.6	15.9169			27.6	27.4177		
18.7	16.0166	23.1	20.9840	27.7	27.5784	32.1	35.5186
18.8	16.1168	23.2	21.1110	27.8	27.7399	32.2	35.7201
18.9	16.2176	23.3	21.2388	27.9	27.9023	32.3	35.9226
19.0	16.3189	23.4	21.3672	28.0	28.0654	32.4	36.1261
		23.5	21.4964			32.5	36.3307
19.1	16.4208	23.6	21.6262	28.1	28.2294	32.6	36.5363
19.2	16.5233	23.7	21.7567	28.2	28.3942	32.7	36.7429
19.3	16.6263	23.8	21.8879	28.3	28.5599	32.8	36.9505
19.4	16.7299	23.9	22.0198	28.4	28.7265	32.9	37.1592
19.5	16.8341	24.0	22.1524	28.5	28.8939	33.0	37.3689
19.6	16.9388			28.6	29.0622		
19.7	17.0441	24.1	22.2857	28.7	29.2313	33.1	37.5796
19.8	17.1499	24.2	22.4196	28.8	29.4013	33.2	37.7914
19.9	17.2563	24.3	22.5543	29.9	29.5722	33.3	38.0042
20.0	17.3632	24.4	22.6898	29.0	29.7439	33.4	38.2180
		24.5	22.8259			33.5	38.4329
20.1	17.4707	24.6	22.9628	29.1	29.9165	33.6	38.6488
20.2	17.5789	24.7	23.1003	29.2	30.0900	33.7	38.8657
20.3	17.6877	24.8	23.2386	29.3	30.2644	33.8	39.0837
20.4	17.7971	24.9	23.3777	29.4	30.4396	33.9	39.3027
20.5	17.9071	25.0	23.5174	29.5	30.6157	34.0	39.5228

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